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CO-PROCESSING OF GRINDING SLUDGE AS ALTERNATIVE RAW MATERIAL IN CEMENT PRODUCTION

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การใช้ของเสียจากอุตสาหกรรมเป็นวัตถุดิบทดแทนหรือทางเลือกในอุตสาหกรรมปูนซีเมนต์นั้นนิยมใช้อย่างชัดเจนในหลายประเทศทั่วโลก ของเสียอันตรายที่ใช้ในกระบวนการผลิตปูนซีเมนต์นั้นมีวัตถุประสงค์เพื่อ เป็นการอนุรักษ์ทรัพยากรที่ใช้แล้วหมดไป เป็นการประหยัดพลังงานเชื้อเพลิง ช่วยทำลายสารที่มีความเป็นพิษ และเป็นการเพิ่มรายได้เชิงเศรษฐศาสตร์ วัตถุประสงค์ของงานวิจัยนี้ คือ การศึกษาความเป็นไปได้ในการนำกากของเสียจากอุตสาหกรรมตัดแต่งชิ้นงานโลหะมาเป็นวัตถุดิบทดแทนในกระบวนการผลิตปูนซีเมนต์ วิธีการศึกษาประกอบด้วย การศึกษาลักษณะของวัตถุดิบในการผลิตปูนซีเมนต์และกากของเสียจากอุตสาหกรรมเจียรชิ้นงานโลหะ การหาสภาวะที่เหมาะสมในการสังเคราะห์ปูนเม็ด การศึกษาผลกระทบของการใช้กากของเสียจากอุตสาหกรรมตัดแต่งชิ้นงานโลหะที่มีต่อคุณสมบัติของผลิตภัณฑ์ปูนซีเมนต์ และการศึกษารูปแบบการชะละลายของโลหะหนักจากจากก้อนซีเมนต์ มอร์ต้า ตัวอย่างในการทดลองประกอบด้วย ตัวอย่างอ้างอิงที่ไม่ผสมกากของเสียและตัวอย่างที่มีการผสมกากของเสียที่ร้อยละ 1 ร้อยละ 2 และ ร้อยละ 3 จากการศึกษาพบว่า ลักษณะของวัตถุดิบมีค่าของ แคลเซียม อลูมินา และ เหล็ก อยู่ในเกณฑ์ปกติ ปริมาณโลหะหนัก ได้แก่ เหล็ก แคดเมียม โครเมียมและนิกเกิล ในตัวอย่างกากของเสียนี้มีอยู่สูงมากจนทำให้กากของเสียนั้นเป็นกากของเสียอันตราย การที่ปริมาณของเหล็กมากนั้นทำให้กากนั้นทำให้กากของเสียนี้จัดเป็นวัตถุดิบทดแทนในอุตสาหกรรมปูนซีเมนต์ได้ สภาวะที่เหมาะสมในกระบวนการสังเคราะห์ปูนซีเมนต์ที่ผสมกากของเสียนั้นคือ ที่อุณหภูมิการเผา 1400 องศาเซลเซียสและเวลาในการเผาที่ 60 นาที ปริมาณการแทนที่ของกากของเสียได้มากที่สุด คือ ร้อยละ 2 การแทนที่กากของเสียในวัตถุดิบที่มากขึ้นนั้น พบว่า ช่วยปรับปรุงความสามารถในกระบวนการเผา ลดการสร้างของไดแคลเซียมอลูมิเนต ทำให้ค่าอัตราส่วน SR และ AR ลดลงแต่ช่วยส่งเสริมการสร้างไตรแคลเซียมซิลิเกตและเตตระแคลเซียมอลูมิเนตเฟอร์ไรต์ การศึกษาโครงสร้างขนาดเล็กของตัวอย่างปูนเม็ดสังเคราะห์แสดงให้เห็นว่า การใช้กากของเสียชนิดนี้ ช่วยให้ไดแคลเซียมซิลิเกตมีขนาดใหญ่ขึ้น สีของไตรแคลเซียมซิลิเกตเข้มขึ้น และพบการเกิดผลึกของไดแคลเซียมซิลิเกตบนไตรแคลเซียมซิลิเกต ผลการศึกษาตัวอย่างปูนเม็ดสังเคราะห์ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดบ่งชี้ว่า เตตระแคลเซียมอลูมิเนตเฟอร์ไรต์เกาะติดอยู่กับไตรแคลเซียมซิลิเกต และโลหะหนักหรือสารอื่นๆพบอยู่ในไดแคลเซียมซิลิเกต โครเมียม ทองแดง และ นิกเกิล มีระดับในการรวมตัวในตัวอย่างปูนเม็ดมากกว่าร้อยละ 90 ผลการศึกษาระดับในการรวมตัวของโลหะหนักในตัวอย่างปูนเม็ดสอดคล้องกับงานวิจัยก่อนหน้านี้ ในการทดสอบการชะละลายตามกฎหมายพบความเข้มข้นของโลหะหนักต่ำกว่าค่ามาตรฐานที่กฎหมายกำหนด การศึกษาการสกัดแบบลำดับพิสูจน์ได้ว่าโลหะหนักในปูนซีเมนต์มีพันธะเคมีที่แข็งแรงกับซิลิกาทำให้ยากที่จะชะละลายออกมาสู่สิ่งแวดล้อมได้ สำหรับรูปแบบการชะละลายของเกลือในตัวอย่างปูนซีเมนต์นั้นเป็นแบบการแพร่ ส่วนรูปแบบการชะละลายของโลหะหนักได้แก่ แคดเมียม โครเมียม นิกเกิล และแคลเซียม เป็นแบบการชะละลายที่ผิวหน้าของตัวอย่างก่อนที่เกิดกระบวนการแพร่ตามมา โลหะหนักที่มีโอกาสชะละลายออกมาได้สูงสุดจากก้อนมอร์ต้าที่การแทนที่ร้อยละ 2 นั้น คือ นิกเกิล ส่วนโลหะหนักที่มีโอกาสชะละลายออกมาได้น้อยที่สุดจากก้อนมอร์ต้า คือ แคดเมียม

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THANTIP PUNMATHAREITH: CO-PROCESSING OF GRINDING SLUDGE AS ALTERNATIVE RAW MATERIAL IN CEMENT PRODUCTION. THESIS ADVISOR: ASST. PORF. MANASKORN RACHAKORNKIJ, Ph.D., THESIS CO-ADVISOR: PROF. METHI WECHARATANA, Ph.D., THESIS CO-ADVISOR: ASST.PROF. APICHAT IMYIM, Ph.D., 221 pp.

Utilization of industry wastes as alternative raw materials in the cement industry is a reality in several countries around the world. Waste streams from the industry are usually employed in the Portland cement production in order to preserve non-renewable resource, save energy cost, destroy toxic substances, and accrue economic incomes through waste management service. This research aims to investigate the potential of partial substitution of cement raw meal with grinding sludge in Portland cement clinker production. Research methodology involves determination of characteristics of cement raw meal and grinding sludge and optimal burning condition for clinker synthesis. It also addresses the effect of grinding sludge on properties of the synthesized clinker and leaching behavior of heavy metals from synthesized Portland cement mortar. One reference and three modified mixtures, containing 1%, 2%, and 3% of dry weight of grinding sludge were examined. XRF analysis results showed that CaO, SiO_2, Al_2O_3, and Fe_2O_3 in ordinary cement raw meal were within typical concentration ranges. The grinding sludge had high concentrations of iron, cadmium, chromium, and nickel and thus it was classified as a hazardous waste. High Fe_2O_3 made the grinding sludge a good candidate for alternative raw material. Optimal burning condition for synthesized Portland cement clinker was found at 1400 °C and 60 minutes. The maximum substitution of grinding sludge was found to limit at 2 % of grinding sludge. The higher replacement of grinding sludge was found to improve burnability, reduce formation of C_2S and C_3A, lower silica and alumina ratios, but promoted the formation of C_3S and C_4AF. Microstructural analysis of the synthesized Portland clinker revealed that the grinding sludge promoted formation of secondary C_2S as well as caused color change of C_3S. SEM analysis also showed incorporation of C_4AF into C_3S and heavy metals into C_2S. Incorporation of heavy metals including chromium, copper and nickel were more than 90% of total content. Regulatory leaching procedure was performed on the synthesized clinker and mortar samples and the heavy metals in the leachate were found below the concentration limits. Sequential extraction revealed strong chemical bonding between heavy metals and silica oxide in the hardened samples that might limit their releases into the environment. The leaching behavior of salts in cement mortar with 2 % of grinding sludge was controlled by diffusion mechanism while the leaching behavior of calcium, cadmium, chromium, and nickel were surface wash-off and diffusion mechanism. The metals with highest leaching potential from synthesized the cement mortar was nickel and the lowest was cadmium.

Field of Study : Environmental Management Student's Signature Thantip Punmatharith
Academic Year : 2009 Advisor's Signature
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NOMENCLATURE

A = Aluminum oxide

Al = Aluminum

Al_2O_3 = Aluminum Oxide

ANC = Acid neutralization capacity test

As = Arsenic

ASTM = American Society for Testing and Materials

C = Calcium oxide

Ca = Calcium

C_2S = Dicalcium Silicate or Belite

C_3S = Tricalcium Silicate or Alite

C_3A = Tricalcium Aluminite

C_4AF = Tetracalcium Aluminoferrite

$CaCO_3$ = Calcium Carbonate or Portlandite

Cd = Cadmium

CO = Carbon Monoxide

CO_2 = Carbon Dioxide

Cr = Chromium

Cu = Copper

DI = Deionized Water

DIW = Department of Industrial Works

F = Iron Oxide

Fe = Iron

Fe_2O_3 = Iron Oxide

HCl = Hydrogen Chloride

HF = Hydrogen Fluoride

Hg = Mercury

ICP-OES = Inductively Coupled Plasma Optical Emission Spectroscopy

K = Postasium

Li = Lithium

L/S ratio = Liquid/solid ratio

Mg = Magnesium

Mn = Manganese

ML = monolithic test or tank test

Na = Sodium

Ni = Nickel

OM = Optical microscope

PC = Portland cement

PCD = Department of Pollution control

Pb = Lead

PW = Pore water test

SEM/EDS = Scanning Electron Microscopy/ Energy Dispersive Spectroscopy

TCLP = Toxicity Characteristic Leaching Procedure

US EPA = United state Environmental protection agency

V = Vanadium

WET = Wet extraction test

XRD = X-ray Diffraction Spectroscopy

XRF = X-ray Fluorescence Spectroscopy

Zn = Zinc

Model abbreviation

A = monolith/eluate exchange surface (m^2)

C = concentration of soluble species (mol/l)

D: =observed diffusion coefficient (m^2 s^{-1})

h = monolith high (m)

k =kinetic constant (s^{-1})

k_t =mass transfer coefficient at the interface of the specimen (m.s-^{1})

Q = leachant renewal flow rate (m^3/s)

S =concentration of a solid phase (mol/L)

Ti =flux representation time (s)

t =time (s)

V = volume of leachant (m^3)

x = distance (m)

z =ion charge

Φ = porosity of the specimen

’ = concentrations in the eluate

eq = at equilibrium

I =at the inlet of reactor

\+ =for catio

\- =for anion

CHAPTER I

INTRODUCTION

1.1 Research Motivations

One of the most important environmental issues in developing countries around the world is poor waste management. Traditional waste management includes illegal dumping of wastes at unsuitable locations, or disposal in ill-designed or mismanaged landfills. Compositions of wastes contain chemicals that may be both nontoxic and dangerous compounds. Highly toxic substances can cause serious contamination of soil, water, and the atmosphere that lead to endangerment of all living organisms. More specifically, they can enter the food chain and affect human and animals.

Increased concern regarding waste management in Thailand has been placed on hazardous waste management. The new waste management notification was enacted by Department of Industrial Works, Ministry of Industry on 2006. This notification increased liability of waste generator, waste transporter, and waste treatment company. Both non-hazardous and hazardous wastes have been addressed in this notification using six-digit waste codes to classify wastes into groups and identify proper management alternatives (DIW, 2005).

Traditional hazardous waste disposal in a secure landfill has its downfalls. First, it faces the problem of attaining public approval, which limits the amount of area available for this method (Espinosa and Teńorio, 2000; Lin and Lin, 2005; Shin et al., 2005). Furthermore, the operation of a secure landfill incurs high investment costs, which makes its hazardous waste management costs relatively high. Many industries are, therefore, in need of a lower cost alternative or one that could generate economic benefit (Raupp-Pereira et al., 2007).

Alternative waste treatment technologies such as incineration and co-processing help to address these issues. Despite the fact that both techniques employ a burning process to reduce the amount and volume of hazardous waste, they are significantly different. Incineration produces highly toxic ash that requires a further treatment process, such as stabilization/solidification, before it can be dumped into a secure landfill (Shin, Chang and Chiang, 2003; Trezza and Scian, 2007). Co-processing, on the other hand, works toward waste minimization and saves natural resources by utilizing wastes or by-products as raw materials or fuel in production processes (Mokrzycki, Uliasz-Bocheńcyk and Saena, 2003; Dalton et al., 2004; Holcim and GTZ, 2006). This technology was first utilized by the cement industry in the 1970s (Benestad, 1989; Kleppinger, 1993); some of the wastes were used as substitutes for main chemical compounds in the raw materials, such silica, alumina, and iron (Trezza and Scian, 2000 and 2005; Kääntee et al., 2004; Pipilikaki et al., 2005; Frias et al., 2006; Navia et al., 2006; Kolovos, 2006). The use of co-processing in the cement industry continues to this day and allows for easy destruction of organic contaminants such as used oil, contaminated soil, scrap tires, and expired chemicals because of high temperatures of more than 1400°C in cement production, and suitable air pollution technology.

In recent years, there has been an increasing interest in burning of hazardous waste in cement production. The serious discussions of co-processing of hazardous waste in cement kiln were addressed to the impacts of heavy metals on cement product and environmental risk. There are many researches on investigation of the effect of heavy metals oxide on the formation and hydration of Portland cement made from raw mix containing pure heavy metals oxide. Thus, the research to date has tended to focus on effect of utilization of real hazardous waste rather than pure chemical oxides.

1.2 Research Objectives

The main purpose of this study is to investigate the potential of partially substituting ordinary cement raw meal with grinding sludge as alternative raw materials in Portland cement clinker production.

The specific objectives are as follows:

1. To find the optimal conditions for synthesis of Portland cement clinker from cement meal, which is mixed with grinding sludge.
2. To analyze chemical compositions, mineralogy, burnability and microstructure of synthesized Portland cement clinker.
3. To understand the mechanism of heavy metals in synthesizing Portland

cement clinker with heavy metals content.

4. To estimate the environmental risk of cement product by regulatory leaching procedure such as wet extraction test (WET) and toxicity characteristic leaching procedure (TCLP).
5. To study the fixation of heavy metals on the formation of clinker and the hydration cement via sequential extraction test.
6. To determine the leaching model of heavy metals in co-processed mortar by employing results from pore water test (PW), acid neutralization capacity (ANC), and monolithic leaching test (ML).

1.3 Hypotheses

The grinding sludge can be used as alternative raw materials in cement production

1.4 Scopes of study

This study was divided into three parts: raw material analysis, distribution of heavy metals in Portland cement clinker and leaching behavior of heavy metals on cement product.

The raw material analysis contained of raw meal analysis and grinding sludge analysis. The analysis consisted of physical and chemical properties. The raw material was randomly collected from local cement company. The raw material was measured the chemical composition by X-ray fluorescence spectroscopy (XRF). The grinding sludge received from waste collector company. The sludge testing composed of heating value, total heavy metals, chloride content, sulfur content, chemical composition, and pH. The raw materials and grinding sludge was mixed. The grinding sludge was substituted with raw material at 0%, 1%, 2% and 3% (w/w) of sludge. The mixed sample was used in distribution of heavy metals in Portland cement (PC) clinker and leaching behavior of heavy metals on cement mortar.

The distribution of heavy metals in PC clinker divided into two sections. The first part was synthesis of PC clinker and the secondary part was analysis of heavy metals in cement product. The synthesis PC clinker must find the optimal burning condition including temperature and time. The PC clinker properties were used to decision of optimal temperature. The main properties were applied in this section contained free lime content, chemical composition, and mineralogical composition. To understand the heavy metals distribution in cement product, the synthesized PC clinker at optimal burning temperature analyzed microstructure via optical microscope and scanning electron microscope with energy dispersive spectroscopy (SEM/EDS) and incorporation of heavy metals by digestion and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Before starting leaching experiments, the synthesized Portland cement clinker for the first part was grinded with 5% of gypsum for preparing of mortar follow ASTM standard and cured 28 days. In addition, the compressive strength at 7, 14, and 28 curing days was tested follow ASTM standard.

The leaching behavior of heavy metals on cement product included regulatory leaching test, sequential extraction, pore water test (PW), acid neutralization capacity test (ANC), and monolithic leaching test (ML). The cement product composed of clinker, cement paste, and cement mortar. To predict environmental risk in short time, the regulatory leaching test used wet extraction test (WET) and toxicity characteristic leaching procedure (TCLP). To understand the chemical formation and heavy metals speciation in cement product, the sequential extraction contained five fractions such as exchangeable, carbonate, iron- manganese oxide, organic matter /sulfide, and residual fraction. To clearly release of heavy metal and leaching behavior in cement mortar, the mathematic model applied with the leaching procedure including pore water test (PW), acid neutralization capacity test (ANC), and monolithic leaching test (ML). The pore water test (PW) was determined the initial equilibrium composition of the pore solution and the soluble species maximum mobile fraction (MMF) for leaching. The acid neutralization capacity test (ANC) was applied from the European pre- standard and used to study the influence of pH on the leaching capacity of inorganic constituents from co-processed cement. The monolithic leaching test (ML) was measured the leaching behavior under dynamic condition and used to explain the dominant release mechanisms of inorganic constituents from co-processed cement. The mathematic model and leaching results was calculated by MATLAB.

1.5 Excepted Results

- Be able to find the optimal burning condition for synthesized PC clinker.
- To understand the effects of grinding sludge on cement properties.
- To understand the mechanism of heavy metals in cement product.
- To understand the leaching of heavy metals from cement product.
- To understand the leaching behavior of heavy metals on cement mortar.

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEWS

All information summarized in this chapter provides the whole picture of theoretical backgrounds. This chapter reviewed overview knowledge as below:

2.1 Cement manufacture
2.2 Chemical composition of Portland cement
2.3 Hydration of Portland cement
2.4 Strength of Concrete
2.5 Leaching procedure
2.6 Co-processing in cement production
2.7 Alternative fuel and raw materials (AFRs)
2.8 Iron industry and grinding sludge
2.9 Heavy metal
2.10 Heavy metal in cement

2.1 Cement manufacture

Portland cement defines as a hydraulic binder or a finely ground inorganic material. It forms a paste and set hardness when it mixes with water and occurs hydration reaction. Hydration reaction retains its strength and stability under water condition (ENV197-1, 1995). The American Society for Testing and Materials standard (ASTM C219-94, 1994) describes as the hydraulic cement produced by pulverizing Portland cement clinker and containing calcium sulfate. The Portland cement clinker is made by burning process of a specified mixture of raw materials. It is a partially fused clinker consisting primarily of hydraulic calcium silicates.

Cement commonly describes as a material with adhesive and cohesive properties which make it capable of bounding mineral fragments into a compact whole. The cement make primary from calcareous materials such as limestone or chalk, alumina, silica, and iron ore. Generally, the raw materials for cement production are found in nearly cement plant. The new cement production is required to reduce energy consumption and decrease employment. The development is achieved in burning and grinding process, the automatic control in all production processes, and the air pollution control. The problems of air pollution are limited by the utilization of alternative raw material and fuel. Also, the replacement of alternative fuel decreases the using of classical fuel as coal and fossil fuel. It helps to reduce of total CO_2 emission from the combustion process. Moreover, the alternative raw materials and fuel have proved that the emission of hazardous gases is lower in comparison with classical fuels. Also, the cement kilns can apply for the destruction of hazardous wastes instead of incinerator and the neutralization and destroy of air pollution substances is more effective. All these reasons show that the cement industry is a friendly environmental business. The processes cement production was shown in Figure 2.1.

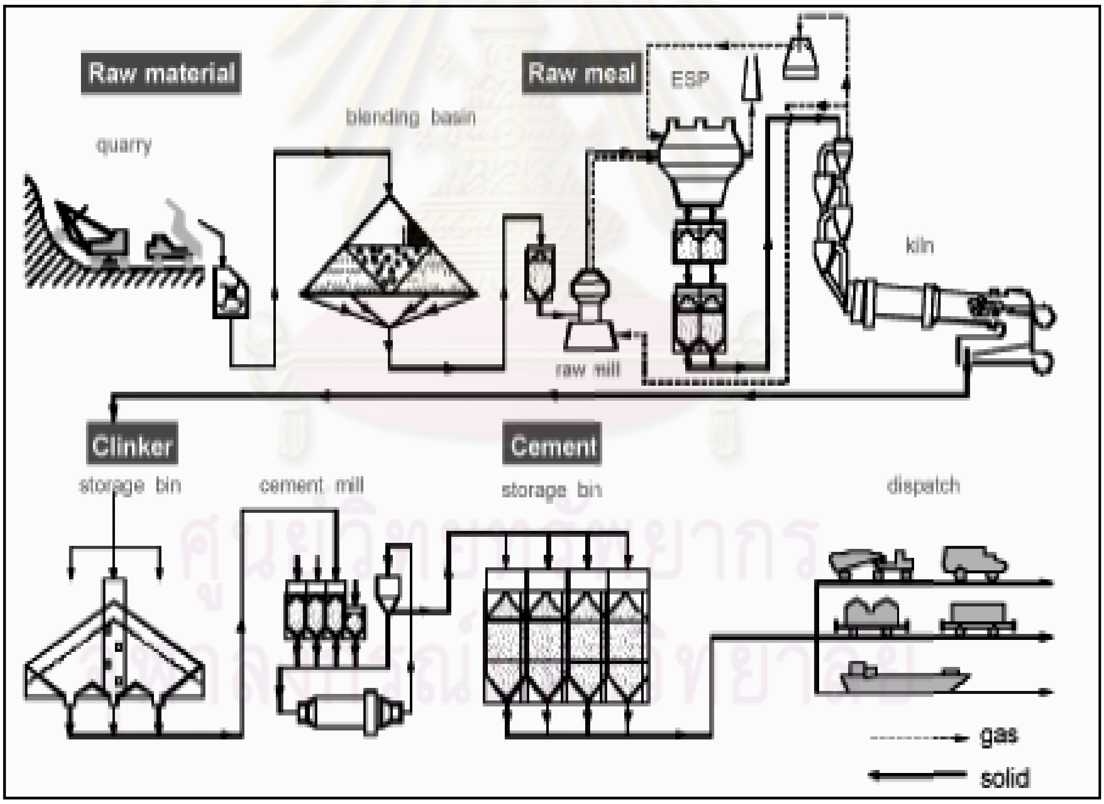


Figure 2.1 Cement manufacturing process (GTZ and Holcim, 2006)

2.1.1 Raw material preparation

The quality and quantitative of Portland cement is estimated by the chemical and mineral composition of Portland cement clinker. The traditional Portland cement clinker has the following mineralogical composition as given in Table 2.1. The share of main oxides is equal to approximately 95 percent and their content is as follows on Table 2.2

Table 2.1 The main chemical composition formula and percentage present in Portland cement clinker (Bensted and Barnes, 2002; Neville, 2003)

Chemical Name	Chemical Formula	Percentage in Portland cement clinker
tri-Calciumsilicate or alite	3.CaO.SiO_2 or C_3S	55-65%
di-Calciumsilicate or belite	2.CaO.SiO_2 or C_2S	15-25%
tri-Calciumaluminate or celite	3.CaO.Al_2O_3 or C_3A	8-14%
tetra-Calciumaluminateferrite or Browmillerite	4.CaO.Al_2O_3. Fe_2O_3or C_4AF	8-12%

Table 2.2 The percent of main oxides in Portland cement clinker (Bensted and Barnes, 2002; Neville, 2003)

Main oxide	General range use, % (w/w)
CaO	60-70 %
SiO_2	18-22 %
Fe_2O_3	2-4 %
Al_2O_3	4-6 %
Other miner chemical compounds (MgO, K_2O, TiO_2, Mn_2O_3, and SO_3)	Less than 5 %

The modulus equations are the most important parameters in order to simplify the control of the chemical composition of raw meal. The commonly equation including lime saturation factors (LSF), Silica Ratio (SR), and Alumina Ratio (AR) are expressed in Table 2.3. For Table 2.3, the ratios occurring were use in Thai cement company. If the AR is lower than 0.64, the clinker does not contain the C_3A

phase but only C_4AF and C_2F and the content of the latter increases with the lowering of AR.

Table 2.3 Modulus equations (Bensted and Barnes, 2002)

Modulus parameter	Equation	Highest Value	Lowest Value
Lime saturation factor (LSF)	$CaO/(2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3)$	1.02	0.9
Silica Ratio (SR)	$SiO_2/(Al_2O_3+Fe_2O_3)$	3.0	2.0
Alumina Ratio (AR)	Al_2O_3/Fe_2O_3	4.0	1.0

2.1.2 Raw material crushing

The primary size reduction of raw materials from quarry process mainly employed the single and twin rotor hammer crusher and impact crushers. The combination process was applied jaw crushers, roll crusher and gyratory crushers. In the limestone quarry, a mobile installation is often applied which provides the economical solution.

2.1.3 Raw material grinding

The main objective of the grinding process is to ensure the suitable raw meal granulometric composition. According to wet and dry grinding of the raw materials, ball mill are used which operate either as open circuit mill or in close circuit, in case of the dry process with on air classifier.

2.1.4 Classifiers

Traditionally, two kinds of separators were applied the so-called grit separator and mechanical separators. Air-swept mills are normally equipped with a grit separator and cyclone. Grit separators have not moving parts and the separation effect is due to diminishing of dust entrained air and its tangential flow induced by guide vanes. The main part of the mechanical separator is a rotating dispersion plate and two fans as the main fan and auxiliary fan.

2.1.5 Homogenization

Raw material homogenization is a very important technological operation because of the stability of chemical composition of kiln feed. The variations of chemical composition of raw mix cause unfavorably the kiln exploitation and clinker quality. According to a stable kiln operation, the lime saturation factor fluctuation should be lower than one point.

2.1.6 Clinker burning

The dry process is predominant in cement industry because of using low heat consumption. The dry process can reduce fuel cost by using of alternative fuels. The development of dry kilns was the introduction of precalcination in the 1970s.This technology needs an important increase of kiln. There are two types of precalcining technology such as partial and total calcination. The degree of calcinations in precalciner is higher than 90-95 percent. The temperature was control in precalciner. If too high temperature is used in precalciner, it causes the heat loss with exit gases and the possibility of a clinkering process starting in the calciner and leading to the formation of product which can block the inlet of the gases supplied from the kiln. The best cement kiln is given very quick reactions, run without recrystallization phenomena and obtained a high hydraulic activity of the clinker.

2.1.7 Coolers

The important of clinker coolers used for reducing of heat in the kiln and cools clinker production. There are three types of coolers which are commonly used: rotary coolers, planetary coolers and grate coolers. Grate coolers are the most common cooler because they ensure the lowest clinker temperature and highest kiln capacity. Planetary coolers take second place because they are mounted on the kiln. Rotary coolers are rarely used because it has a limited air flow. The most favorite cooler is the grate coolers because it can quickly decrease temperature in Portland cement clinker, but they still produce a lot of exit hot air. The best solution is to use the exit hot air for drying raw materials, slag and coal or produce electrical energy.

2.1.8 Cement grinding

The Portland cement clinker is generally fed to a store to measure properties or quality control and also to cool at ambient temperature. After that, the calcium sulfate or gypsum rock was added to the clinker in amount normally between 3 and 8 percent. The gypsum rock retards the hydration of tricalcium aluminate and to optimize the strength of properties of the calcium silicate.

The ball mill is more frequently used for cement grinding. The modern mill is two chamber mills with lifting liner in the first and classifying liner in the second compartment. Significant progresses in grinding technology have been due to the application of roller press for pre-grinding or finish grinding.

2.1.9 Cement testing and control

The results from this step were used to control all operation system in cement production. The main compounds were calculated by Bogue and Modulus equations. These calculations explained in two difference meanings, notably as potential values or realistically operation system. The significance of this step will display the quality and quantitative present in kiln.

2.2 Chemical composition of Portland cement

Cement component are generally explained by their phase relations out of phase diagram determination. The utilization of alternative raw material and fuel in cement production effects to cement system and complex phase of cement minerals. For instance, the use of alternative raw materials and fuel causes phase change or formation of new phases. Some amount of addition phases which can occur due to increasingly used impure raw and secondary materials cannot be found direct by X-ray method, but must also be identified by different addition method. Despite the knowledge of phase formation and crystallization condition derived from phase diagram, a description and investigation of clinker and phase formation requires different methods. The comparison of the advantage and disadvantage of some determination method are summarized in Table 2.4

According to the main chemical compound of raw material in the Portland cement production, these compound combined and from a series of more complex productions such as C_3S, C_2S, C_3A, and C_4AF. The amount of complex products or crystalline materials present in the cooled clinker.

The silicates in cement are not the pure compound, but usually contain minor oxides in solid solution. These oxides cause the atomic arrangement, crystal form and hydraulic properties of the silicates.

The calculation of potential composition of Portland cement is based on the work of R.H. Bogue and others. It is often referred to as “Bogue composition”. Bogue equations for the percentages of main compounds in cement are given oxide in the total mass of cement. It was expressed in Table 2.5.

Table 2.4 Comparison of Bogue, microscopy and X-ray techniques for phase determination (Pöllmann et al., 1997)

Determination Method	Preparation	Measurement	Calculation	Precision	Advantage	Disadvantage
Optical Microscopy or Scanning electron microscopy (SEM)	Crushing; embedding in epoxy resin; polishing; surface etching (high personnel expense; no automation; time consumption 2 days)	Visual investigation; description of the microstructure (well educated and trained personnel necessary high time consumption (1 day); no automatization)	Calculation of vol% into mass (table calculator)	Standard deviation of about 2%	quantification and microstructure simultaneously; information on clinker genesis and crystal shape and size	High time consumption; high preparation effort; well trained worker necessary; no automatization possible
X-ray diffraction Method	Grinding; sample preparation (low personnel and equipment effort; automatization; time consumption 20 minute)	PC-controlled XRD (high equipment effort; automatization possible; time consumption calculation 1 hour)	Quantification with a PC program automation calculation within 1 minute	Absolute error of 1 mass%	Exact results on phase consumption no texture effects; standardless; additional information on minor phase	High measuring time; only quantification data
Bogue calculation	Grinding; powder/glass pellets preparation (low personnel and equipment effort; automatization; time consumption 20 minute)	XRF analysis; wet analysis of volatile compound and of free lime (XRF automatically; measurement time calculation 5 min; wet analysis need high personnel and time effort)	Normative phase quantification from chemical analysis (automatic calculation)	Depends on the phase composition	Fast and automatic analysis; within defined phase consumption good quantification results	Only normative phase; quantification; wet analysis necessary for exact quantification

Table 2.5 Bogue equations (Neville, 2003)

Bouge parameter	Equation
C_3S	$4.07CaO-7.60SiO_2-6.27Al_2O_3-1.43Fe_2O_3-2.85SO_3$
C_2S	$2.87\ SiO_2-0.75C_3S$
C_3A	$2.65Al_2O_3-1.69Fe_2O_3$
C_4AF	$3.04\ Fe_2O_3$

There exist minor compound such as MgO, TiO_2, Mn_2O_3, K_2O, and Na_2O. The oxides of sodium and potassium knew as the alkalis. They were found to react with some aggregates, observed to affect the role of gain of strength of cement.

The relationship of simple oxide in cement chemistry is occurred by the free lime content. High free lime content has been indicated the burning condition or homogenization in cement production. The production at low temperature cause high free lime in clinker product. Free lime and free magnesium content in clinker are restricted because of the hydration of phase on-expansion reaction.

The chemical reactions that occur in the kiln described a basic understanding of cement how and why it behaves as it does. The temperature is increased when going from the meal feed to the rotary kiln. The most important oxides that participate in the reactions are CaO, SiO_2, Al_2O_3 and Fe_2O_3. These chemicals will combine in to many chemical molecules. Important data on these molecules are summarized as following.

2.2.1 Tricalcium silicate (C_3S) – Alite

C_3S occurs in amount of 50 -90 percent in Portland Cements. It formed above 1250 ºC by a reaction of C_2S and CaO and it can be metastably obtained by rapid cooling of the mixture. The other chemicals highly influence on the formation of C_3S and its polymorphs such as high SO_3 can retard alite formation. C_3S usually show in pseudohexagonal unit cell and can be identified in clinker. A stabilization of polymorphs can be obtained by incorporation of foreign ions in alite-lattice. According to foreign ions and stabilization of C_2S, only small amounts of alkalies are incorporated in C_3S more than in C_2S. The crystal structure of C_3S is composed of

SiO_4-tetrahedra that linked with calcium ions. Calcium is coordinated by eight oxygens. The crystalline structural model is given in Figure 2.2 (a).

2.2.2 Dicalcium silicate (C_2S) – Belite

C_2S may be occurred in 10-40 percent in Portland cement. It can transformation in many range of temperature such as γ-C_2S and β-C_2S. These phases transformation cause the twin lamellae which can be observed in the optical microscope. Belite can incorporate the large amount of foreign ions more than alite. It can occur from many sources. For example, primary belite formed by reaction of lime and silicon sources. Then, secondary belite formed by the decomposition reaction of alite according to the changing of C_3S to C_2S and C and forming small crystals on the rims of alite crystals. Finally, tertiary belite happened from the recrytallization of the interstitial phase coming from the decomposition and decreased solution of SiO_2 in C_3S-phase. The structural model of C_2S is shown in Figure 2.2 (b).

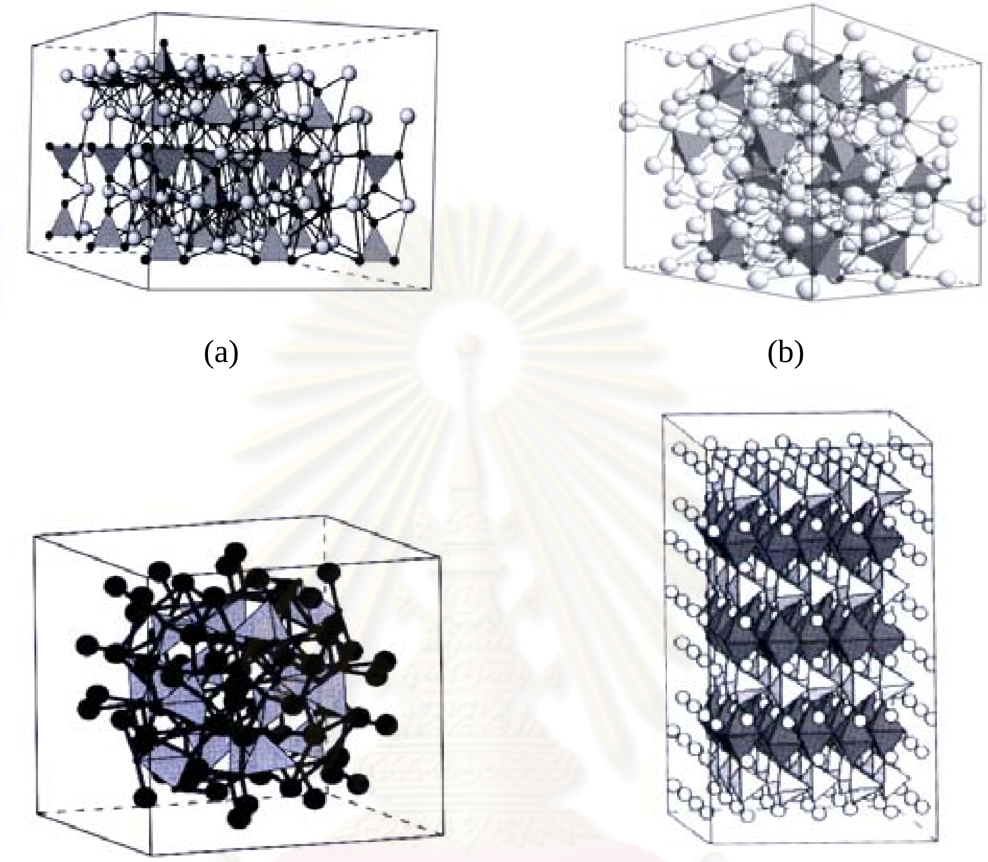
2.2.3 Tricalcium aluminate (C_3A)

C_3A is the most abundant Al-containing phase in Portland cement. According to Ca/Al ratio, the foreign ions can replace in C_3A system. The C3A crystal structure is contained of $(AlO_4)^{5-}$- tetrahedral linked to $(Al_6O_8)^{18-}$ rings which are connected by the Ca^{+2}-ions. So, the foreign ions take place of Ca and the second is located in the centre of the $(Al_6O_8)^{18-}$ rings. The solid solution of C_3A can transform into tetragonal polymorphs (pseudoorthorhombic) at high temperature. The structural model of C_3A is shown in Figure 2.2 (c).

2.2.4 Tetracalcium aluminoferrite (C_4AF)

Iron is commonly fixed under oxidizing conditions in the calcium aluminum ferrite The composite of ferrite phase can be explained by a limited solution between C_2F and C_6A_2F, the crystal structure of C_4AF is contained layers of (Al,Fe)-O_6-octahedral and (Al,Fe)O_4-tetrehegra linked along joint edges. It can call

"Brownmillerite". The structural model of C_4AF is shown in Figure 2.2 (d) (Bensted and Barnes, 2002; Brown, 1948).



(a) (b)

(c) (d)

Figure 2.2 Structure models of major components of clinker: (a) C_3S (b) C_2S (c) C_3A (d) C_4AF (Bensted and Barnes, 2002)

2.3 Hydration of Portland cement

When Portland cement is mixed with water, its composition compound underwent a series of chemical reactions. Reactions with water described as hydration, and the new chemical formed on hydration are collectively referred to as hydration productions. In the case of cement chemistry, it is of interest to know whether the hydration product contribute to the strength of the hydrated cement. The hydration characteristics of the cement compounds are summarized in the Table 2.6.

Table 2.6 Characteristics of hydration of the cement compounds

Compounds	Reaction rate	Amount of heat liberated	Contribution to cement	
			Strength	Heat liberation
C_3S	Moderate	Moderate	High	High
C_2S	Slow	Low	Low initially, high later	Low
$C_3A+C\bar{S}H_2$	Fast	Very high	Low	Very high
$C_4AF+C\bar{S}H_2$	Moderate	Moderate	Low	Moderate

Tricalcium silicate is responsible for most of the early strength (first 7 days). Dicalcium silicate, which reacts more slowly, contributes only to the strength at later times. Tricalcium silicate will be discussed in the greatest detail. The equation for the hydration of tricalcium silicate is given by:

Tricalcium silicate + Water--->Calcium silicate hydrate+Calcium hydroxide + heat

$2\ Ca_3SiO_5 + 7\ H_2O \text{--->} 3\ CaO\cdot 2SiO_2\cdot 4H_2O + 3\ Ca(OH)_2 + 173.6kJ$

Upon the addition of water, tricalcium silicate rapidly reacts to release calcium ions, hydroxide ions, and a large amount of heat. The pH quickly raised to over 12 because of the release of alkaline hydroxide (OH^-) ions. This initial hydrolysis slows down quickly after it starts resulting in a decrease in heat evolved. The reaction slowly continues producing calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Ions precipitate out of solution accelerating the reaction of tricalcium silicate to calcium and hydroxide ions. (Le Chatlier's principle). The evolution of heat is then dramatically increased. The formation of the calcium hydroxide and calcium silicate hydrate crystals provide "seeds" upon which more calcium silicate hydrate can form. The calcium silicate hydrate crystals grow thicker making it more difficult for water molecules to reach the unhydrated tricalcium silicate. The speed of the reaction is now controlled by the rate at which water molecules diffuse through the calcium silicate hydrate coating. This coating thickens over time causing the production of calcium silicate hydrate to become slower and slower.

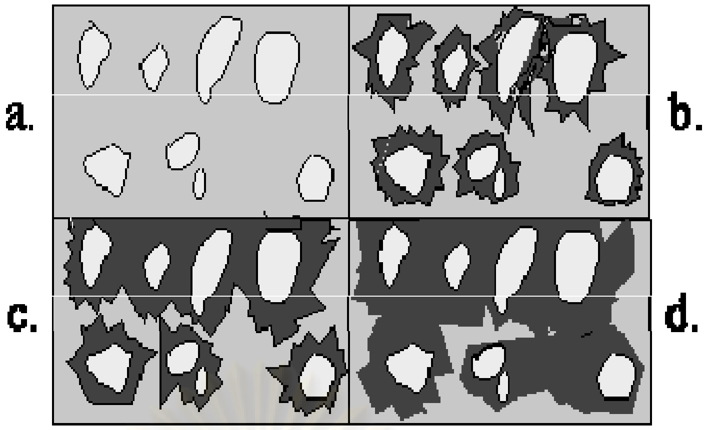


Figure 2.3 Schematic illustrations of the pores in calcium silicate through different stages of hydration.

The above diagrams represent the formation of pores as calcium silicate hydrate is formed. Note in diagram (a) that hydration has not yet occurred and the pores (empty spaces between grains) are filled with water. Diagram (b) represents the beginning of hydration. In diagram (c), the hydration continues. Although empty spaces still exist, they are filled with water and calcium hydroxide. Diagram (d) shows nearly hardened cement paste. Note that the majority of space is filled with calcium silicate hydrate. That which is not filled with the hardened hydrate is primarily calcium hydroxide solution. The hydration will continue as long as water is present and there are still unhydrated compounds in the cement paste.

Dicalcium silicate also affects the strength of concrete through its hydration. Dicalcium silicate reacts with water in a similar manner compared to tricalcium silicate, but much more slowly. The heat released is less than that by the hydration of tricalcium silicate because the dicalcium silicate is much less reactive. The products from the hydration of dicalcium silicate are the same as those for tricalcium silicate:

Dicalcium silicate + Water--->Calcium silicate hydrate + Calcium hydroxide +heat

$2\ Ca_2SiO_4 + 5\ H_2O \text{--->} 3\ CaO \cdot 2SiO_2 \cdot 4H_2O + Ca(OH)_2 + 58.6\ kJ$

The other major components of portland cement, tricalcium aluminate and tetracalcium aluminoferrite also react with water. Their hydration chemistry is more complicated as they involve reactions with the gypsum as well. Because these reactions do not contribute significantly to strength, they will be neglected in this discussion. Although we have treated the hydration of each cement compound independently, this is not completely accurate. The rate of hydration of a compound

may be affected by varying the concentration of another. In general, the rates of hydration during the first few days ranked from fastest to slowest are:
tricalcium aluminate > tricalcium silicate > tetracalcium aluminoferrite > dicalcium silicate.

Heat is evolved with cement hydration. This is due to the breaking and making of chemical bonds during hydration. The heat generated is shown below as a function of time.

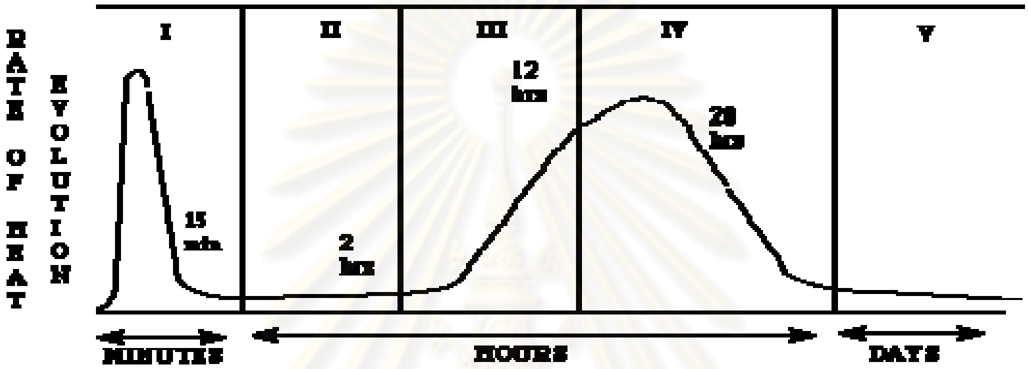


Figure 2.4 Rate of heat evolution during the hydration of portland cement

The stage I hydrolysis of the cement compounds occurs rapidly with a temperature increase of several degrees. Stage II is known as the dormancy period. The evolution of heat slows dramatically in this stage. The dormancy period can last from one to three hours. During this period, the concrete is in a plastic state which allows the concrete to be transported and placed without any major difficulty. This is particularly important for the construction trade who must transport concrete to the job site. It is at the end of this stage that initial setting begins. In stages III and IV, the concrete starts to harden and the heat evolution increases due primarily to the hydration of tricalcium silicate. Stage V is reached after 36 hours. The slow formation of hydrate products occurs and continues as long as water and anhydrate silicates are present.

2.4 Strength of Concrete

The strength of concrete is very much dependent upon the hydration reaction just discussed. Water plays a critical role, particularly the amount used. The strength of concrete increased when less water was used to make concrete. The hydration reaction itself consumes a specific amount of water. Concrete is actually mixed with more water than is needed for the hydration reactions. This extra water is added to give concrete sufficient workability. Flowing concrete is desired to achieve proper filling and composition of the forms. The water not consumed in the hydration reaction will remain in the microstructure pore space. These pores make the concrete weaker due to the lack of strength-forming calcium silicate hydrate bonds. Some pores will remain no matter how well the concrete has been compacted.

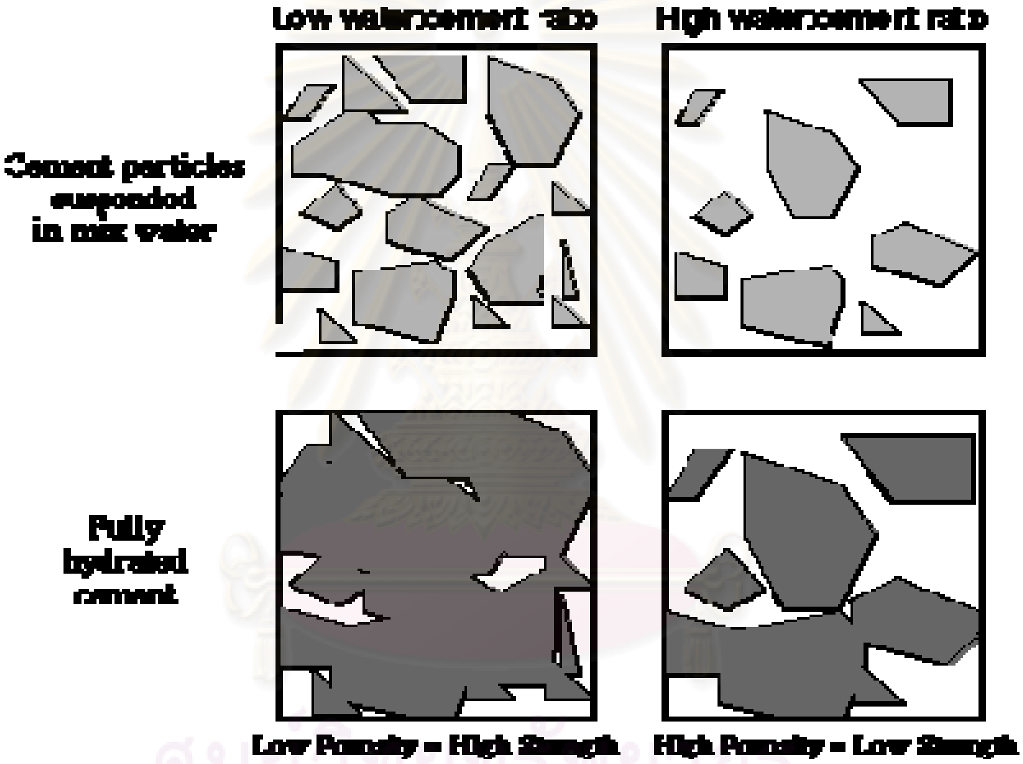


Figure 2.5 Schematic drawings to demonstrate the relationship between the water/cement ratio and porosity.

The empty space (porosity) is determined by the water to cement ratio. The relationship between the water to cement ratio and strength is shown in the graph that follows.

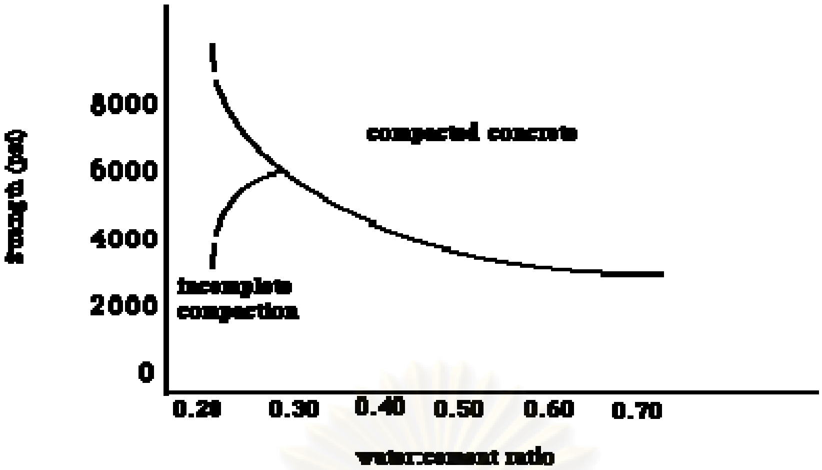


Figure 2.6 A plot of concrete strength as a function of the water to cement ratio.

Low water to cement ratio leads to high strength but low workability. High water to cement ratio leads to low strength, but good workability.

The physical characteristics of aggregates are shape, texture, and size. These can indirectly affect strength because they affect the workability of the concrete. If the aggregate makes the concrete unworkable, the contractor is likely to add more water which will weaken the concrete by increasing the water to cement mass ratio.

Time is also an important factor in determining concrete strength. Concrete hardens as time passes. Why? Remember the hydration reactions get slower and slower as the tricalcium silicate hydrate forms. It takes a great deal of time (even years!) for all of the bonds to form which determine concrete's strength. It is common to use a 28-day test to determine the relative strength of concrete.

Concrete's strength may also be affected by the addition of admixtures. Admixtures are substances other than the key ingredients or reinforcements which are added during the mixing process. Some admixtures add fluidity to concrete while requiring less water to be used. An example of an admixture which affects strength is super-plasticizer. This makes concrete more workable or fluid without adding excess water. A list of some other admixtures and their functions is given below. Note that not all admixtures increase concrete strength. The selection and use of an admixture are based on the need of the concrete user.

2.5 Leaching procedure

Leaching is the process by which inorganic or organic contaminants are released from the solid phase into the water phase under the influence of mineral dissolution, desorption, complexation processes as affected by pH, redox, dissolved organic matter and (micro) biological activity. In many respects leaching behavior as reflected by the pH dependence leaching test and related characterizations leaching tests provides a better means of assessing environmental impact than analysis of total composition.

2.5.1 Type of leaching test

1. pH dependence leaching test

pH is one of the main leaching controlling parameters. The information can be used for geochemical speciation modeling, to evaluate high sensitivity (steep concentration - pH slopes) and to provide information on the sensitivity of leaching under externally imposed changes in pH (natural or caused by treatment) in specific field scenarios. In addition, the test provides a measure of acid/base neutralization capacity (ANC/BNC).

2. Column leaching test

The column test is run in up-flow mode. The leachant is demineralised water (DMW). The test material should have a particle size < 4mm. Seven eluate fractions are collected within the range of L/S = 0.1-10 l/kg. This procedure addresses both inorganic and organic contaminants.

3. Tank leaching test

In the test a monolithic specimen is subjected to leaching in a closed tank to evaluate surface area related release. The leachant demineralised water is renewed after 8 hours and 1, 2, 4, 9, 16, 36, 64 days using a leachant to product volume ratio (L/V) of 5. The results are expressed in mg/m^2.

4. Compacted granular leaching test

This test resembles the tank leach test for monolithic materials in the way it is carried out and the data are handled. The method is designed for granular materials that behave as a monolith in the scenario under investigation (e.g. clay lens in a sandy soil)

Table 2.7 Target and Objectives of leaching test

Types of leaching test	Leaching solution	Target	Objectives
EPA SW 846 METHOD 1311 Toxicity Characteristic Leaching Procedure (TCLP)	0.1M HOAc, pH 2.88 (extraction #2)	To demonstrate in landfill condition.	To determine the mobility of both organic and Inorganic analytes present in liquid, solid, and multiphase wastes.
The Notification B.E 2548 (2005)	0.2 M sodium citrate at pH 5.0 ± 0.1	To evaluation waste before dumping into landfill.	To use for classification hazardous waste.
pH dependence leaching test	Nitric acid and sodium hydroxide.	gives us useful information on the global response of the studied material with regard to an acidic aggression of the medium (alkaline capacity).	to study the influence of pH on the leacheability of inorganic constituents from a waste material by addition of predetermined amounts of acid or base to reach desired end pH values in apparent steady state condition.
Tank Test	DI water	To permits to determine the leaching behavior of monolithic wastes under dynamic conditions.	to determine the dominant release mechanisms of inorganic constituents from regularly shaped specimens of monolithic wastes

2.5.2 Release process of constituents from porous materials

The diffusion is the main process to control the release of constituent from the porous materials, for example concrete, bricks, and coated materials. The released constituent considered on inorganic or heavy metals and the release process depended on materials specific factors and environmental factors. Figure 2.7 was clearly explained overall influential factor on the release of chemical from materials.

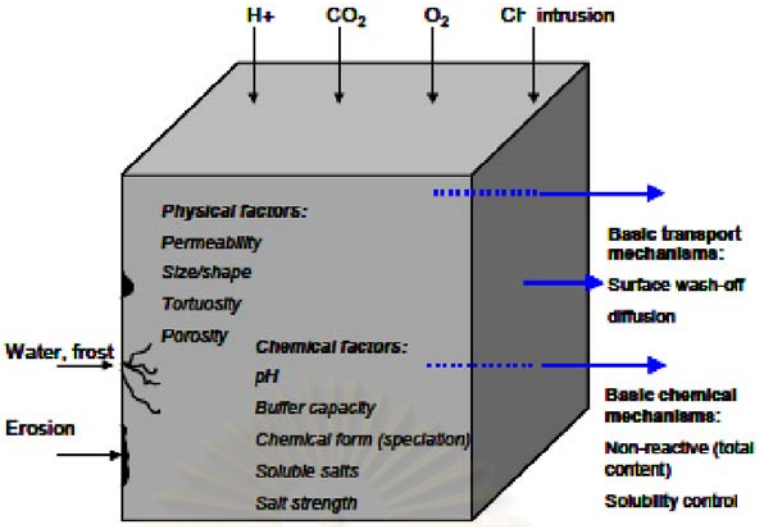


Figure 2.7 Material-specific and release processes

Generally, the release process in aqueous phase was controlled by chemical processes, physical transport processes and external factors.

2.5.2.1 Chemical processes

a) Basic chemical mechanisms

There are three main chemical mechanisms to control the release of constituent from materials, which are dissolution, adsorption, and availability. The dissolution of constituent depended on the solubility, whereas the adsorption process was controlled by affinity to reaction surface or electron exchange. Although, the positive charges of heavy metals are commonly adsorption more than dissolution; the release of heavy metals in nature are controlled by availability. The availability is the total composition of material.

b) pH

The release process of constituent from materials was influenced by pH value of environment and itself. Generally, the leaching behavior of materials as a function of pH divided into three groups including salts, positive charge (cation), and negative charge (anion). Figure 2.8 described the patterns of leaching behavior of element from porous material at different pH values. The actual pH at which leaching takes place, depends on the pH of the material itself, the pH of the surrounding environment and the buffering capacity of the material. Absolute levels are different for each material due to influence of redox, DOC (dissolved organic carbon) and other factors. The leaching patterns of different groups of elements for all sorts of materials are very systematic, but differ in absolute levels. It leads to a "chemical fingerprint" of a material.

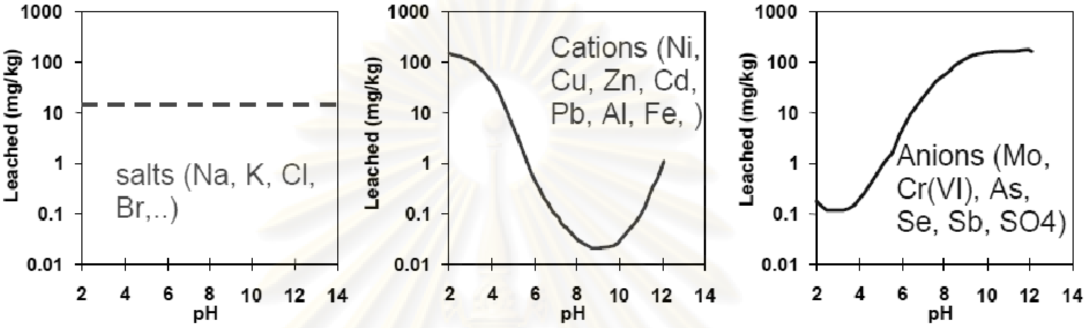


Figure 2.8 Patterns of leaching behavior of element

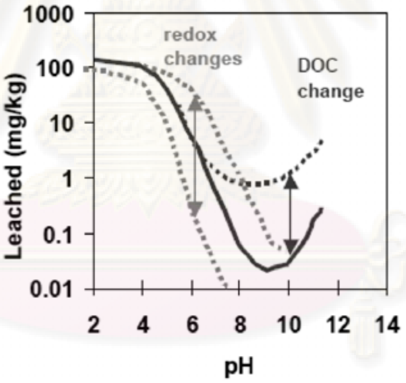


Figure 2.9 Absolute levels and other effects

c) Chemical form of the constituent in the product

Contaminants may be in the oxidized or reduced form, which is important for their leaching behavior. Heavy metals tend to complex strongly with natural substances present in natural waters, soils and natural building products. Complex forms of heavy metals are generally highly soluble and therefore, are released more rapidly than unstable forms of heavy metals.

d) Total composition of the product

The total composition (in the sense of mg of an element per kg of product) has only a limited influence on the maximum leaching of most elements. Exceptions are non-reactive soluble salts, of which the maximum leached amount over time is often similar to the total amount present in the product. The release of other elements is primarily caused by geochemical mechanisms and physical factors, and leached amounts therefore seldom correlate with its total content.

e) Redox reaction

Oxidation /reduction state of the material or its environment ("redox") influences the chemical form of a contaminant. For heavy metals, the oxidation of an initially reduced material usually enhances leached amounts while reduction will have the opposite effect. This relates to the chemical form of the elements of interest.

f) Acid-base buffering

The acid- base buffering capacity of a product determines how the pH develops over time under influence of external factors. Examples are the neutralization of cementitious products due to the uptake of atmospheric carbon dioxide. In such cases, the alkaline buffering capacity of the cement determines the time needed until the pH drops from strongly alkaline (pH > 12) towards a neutral pH value (pH ~ 8).

g) Organic matter and DOC

Solid and dissolved organic matter or humic substances (often expressed as "DOC", dissolved organic carbon) consists of complex molecules that have a high affinity to bind heavy metals. The presence of DOC can enhance leaching by several orders of magnitude (see above). As a result a new partitioning between DOC-bound metal and free metal will be established. DOC is found in natural building products, such as wood. Organic matter is usually present in large amounts in organic environments and in some primary or secondary materials. Even concrete, which is considered as an inorganic material, contains DOC in the form of organic additives used as agents to retard setting.

h) Composition of the water phase and ionic strength

The salt strength of the solution in the product or its environment influences the solubility of other components (generally, a higher salt strength increases the leaching of contaminants). Other components present in the solution may cause enhanced leaching due to complexation, such as metal complexes with chloride or carbonates.

i) Temperature

Temperature increase generally leads to a higher solubility. In addition, an increase in temperature has an increasing effect on chemical reaction rates, and thus also an increasing effect on transport by diffusion.

l) Time

Time is an important factor for the amount released when

1) In general, the time scale that applies to the use of a specific material in a given application;
2) The rate at which processes proceed, which may be limiting for the release in case of slow reaction kinetics (slow dissolution of minerals) or diffusion. It may not be feasible to allow such reactions to run to completion, as the time to reach that stage may be far too long. In that case, one has to estimate the possible consequences of such slow processes on the overall release.
3) The change of material properties or environmental conditions over time. Examples are the carbonation of alkaline products (altering its release properties) or the increased surface area of a monolith due to erosion.

Test methods that include several steps provide insight in the short and long term effects of leaching. Such tests may give information for interpolation or extrapolation towards shorter or longer leaching periods.

2.5.2.2 Physical transport factors

a) Basic transport mechanisms

Three basic transport mechanisms can be distinguished that will be introduced briefly below.

The process of constituents taken along with the water percolating through or along the product is called advection. Water percolating through or along a product is usually caused by rainfall, and plays a major role in the release and impact on soil and groundwater due to the further distribution of the constituents. Percolation *through* a product is only possible for porous materials (such as granular materials).

Diffusion is the transport of constituents solely due to the movement of molecules in the absence of flow. This generally plays a role for compacted materials that have a very low permeability and porosity (the water in the pores will then be stagnant). Still release will occur, but on the basis of transport by diffusion. Under those circumstances, diffusion may be the limiting transport step before constituents can be taken along due to further advection. The rate of diffusion is dependent on the gradient of the constituent between the product and the contacting water phase, and is time dependent. Surface wash-off is a process that is similar to advection. The term surface wash-off is used to define the (initial) wash-off of soluble materials on the outside of monolithic products. After the initial wash-off, diffusion is normally the major transport mechanism in monolithic materials.

b) Granular/monolithic

As mentioned before, it is important to distinguish granular and monolithic products because of the different transport regimes for these two categories. The release behavior due to contact with water is percolation dominated for granular materials and diffusion dominated for monolithic materials (i.e. the amount released depends on the time-dependent diffusion of constituents from the products towards the water phase). For monolithic materials, initial surface wash-off may play a significant role. In that case, soluble salts present on the surface dissolve rapidly and cause an (initial) elevated release.

In some cases, granular material may be compacted or overlain with additional low permeability material in the field, resulting in the granular material also behaving in a manner similar to a monolithic material.

c) Particle size

For granular materials, the particle size determines the distance over which a contaminant must travel from the centre of the particle towards the water phase. Reaction and transport is fast for granular materials with a small particle size. The coarser the grain size, the more the transport tends to be limited by diffusion.

d) Porosity

The pore space or porosity (ratio of pore space and total volume) is a factor that influences the transport rate of constituents towards the water phase both for monolithic and granular materials. Transport of water is easier in media with a high porosity than in a low porosity medium; therefore, a higher porosity generally leads to a higher release.

e) Permeability

The permeability or hydraulic conductivity determines how "easy" water enters the product, and how fast contaminants will be released over time. Permeability may be an issue for dense, clayey materials or monolithic materials. Water tends to flow around products with a low permeability rather than to enter it; this is why products with a low permeability tend to show diffusion-controlled release.

f) Tortuosity

For monoliths showing diffusion-controlled release, a material- specific factor determining the rate of diffusion (effective diffusion) is the tortuosity. It is defined as the ratio between the actual path length, over which a constituent is transported between two points, and the straight line distance between these two points. Materials with a fine channeled, internal pore structure will have a higher tortuosity. This will result in a lower release rate.

g) Monolith size and shape

The quantity of a substance leaching from a product by diffusion depends primarily on the size and the geometry of the product. These factors directly relate to the amount of exposed surface area of the product, which is an important factor for diffusion. Diffusion proceeds faster for products with a high exposed surface area per weight unit.

Diffusion tests and diffusion formulae are primarily based on monolithic specimens that are thick enough to maintain concentrations of available substances in the centre of the specimen at their original level. As soon as in the core of the specimen the available level of constituents decreases ‘depletion’ effects appear in test results. For thin products or highly porous materials this may appear soon, sometimes even in the test itself. In practice, depletion may not occur for hundreds of years. This difference between test performance and practice is important to realize in the interpretation of test results.

h) Sensitivity for erosion

For monolithic materials, physical erosion/abrasion (e.g. influence of water and frost) has an increasing effect of release due to two factors. First, erosion will lead to an increased surface area. Second, due to erosion, new fresh surface is exposed, which leads to a higher gradient of investigated that just transport of all kinds of aggregates and the placement of the aggregates into a road base may lead to more than a doubling of the active surface of the aggregates by the fines created in handling.

i) Salt intrusion

Intrusion (diffusion into the product) of salts (e.g., chloride) into steel-enforced concrete structures may be severely damaging, due to oxidation processes of the steel armor. In advanced stages of the oxidation process, the steel enforced concrete may burst. Fresh area is exposed, and the total area is increased. This leads to a higher release.

2.5.2.3 External factors

Several "external" factors are important for the release behavior under field conditions. Many of them relate to the amount of water to which the product is exposed in a certain time interval, such as the water flow rate (monolithic materials) and the occurrence of preferential flow paths in granular materials. These external factors are dependent on the application scenario (e.g., covered or uncovered product). Other factors that influence the release are e.g. degradation of organic substances in the product, or the degradation of substances due to the influence of light. A summary of factors influencing release is given in Table 2.8.

Table2.8 Summary of the main factors influencing release

Chemical processes	**Physical factors**	**External factors**
- Dissolution - pH - Chemical form -Total composition/ availability - Redox. - Acid-base buffering - DOC - Composition water phase/ionic strength - Temperature - Time	- Percolation - Diffusion - Surface wash off - Granular/monolithic - Size (particles or monoliths) - Porosity - Permeability - Tortuosity - Erosion	- Amount of water, - Contact time - pH of environment - Temperature - Redox of environment - DOC / Adsorption

2.6 Co-processing in cement production

Co-processing refers to the use of waste materials in industrial processes, such as cement, lime, or steel production and power stations or any other large combustion plant. In a few cases this process is also called co-incineration, but we recommend to name it co-processing as the main objective is not the final disposal of waste, but rather the substitution of primary fuel and raw material by waste. It is a recovery of energy and material from refuse (Holcim and GTZ, 2006). The waste hierarchy has to be respected for any waste disposal option, including co-processing. The waste hierarchy (Figure 2.9) has to be respected for any waste disposal option, including co-processing. Co-processing should be considered as a treatment alternative within an integrated waste management concept. Whenever possible, waste should be avoided or used for energy and material recovery, as from the ecological and economical point of view this is the most appropriate solution for any country. However, it may take time to fully implement this approach in developing countries.

Co-processing of waste in cement kilns offers advantages for the cement industry as well as for the authorities responsible for waste management. Cement producers can save on fossil fuel and raw material consumption, contributing to a more eco-efficient production. One of the advantages for authorities and communities is that this waste recovery method uses an existing facility, eliminating the need to invest in a new, purpose-built incinerator or secure landfill site. Co-processing should be considered in any approach to waste management. A detailed systems approach, comparing individual waste technologies and looking at the interface of combined processes (collection, storage, recycling and disposal) will help to optimize waste management from ecological, social and economical points of view. Tools to be applied for this approach are material and energy flux analyses and eco-balances.

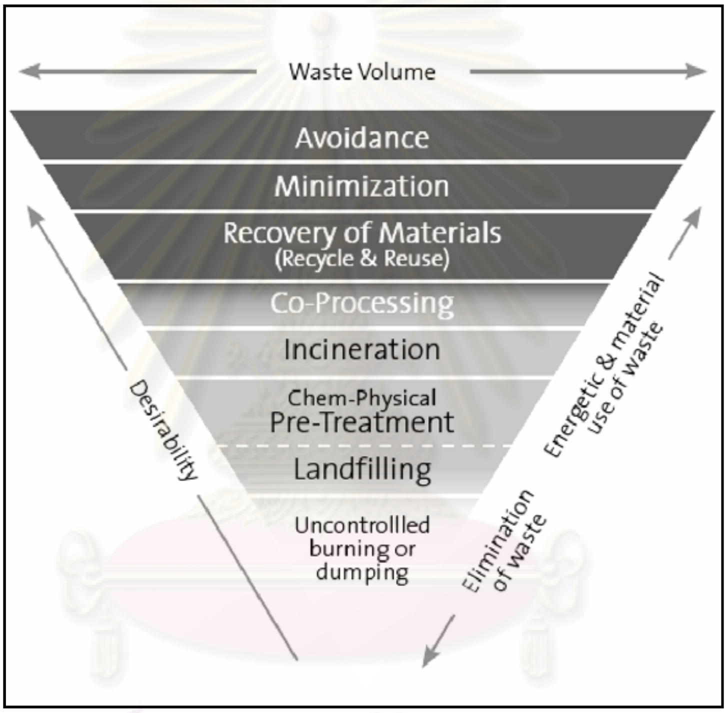


Figure 2.10 Waste management hierarchies (Holcim and GTZ, 2006).

2.7 Alternative fuel and raw materials (AFRs)

Alternative Fuel and Raw Materials or AFRs to waste materials used for co-processing. Such wastes typically include plastics and paper/card from commercial and industrial activities (e.g. packaging waste or rejects from manufacturing), waste tires, waste oils, biomass waste (e.g. straw, untreated waste wood, dried sewage sludge), waste textiles, residues from car dismantling operations, hazardous industrial waste (e.g. certain industrial sludge, impregnated sawdust, spent solvents) as well as obsolete pesticides, outdated drugs, chemicals and pharmaceuticals (Holcim and GTZ, 2006).

The utilizations of AFR usually employ direct and indirect into the cement production process (Figure 2.10). The direct application was suitable with alternative fuel (AF) and the indirect utilization was proper on alternative raw materials (AR). The AF feed commonly via the main burner at the rotary kiln outlet end, a feed chute at the transition chamber at the rotary kiln inlet end, and secondary burners to the riser duct, and precalciner. But, the AR is typically fed to the kiln system in the same way as traditional raw materials including mixing with raw meal.

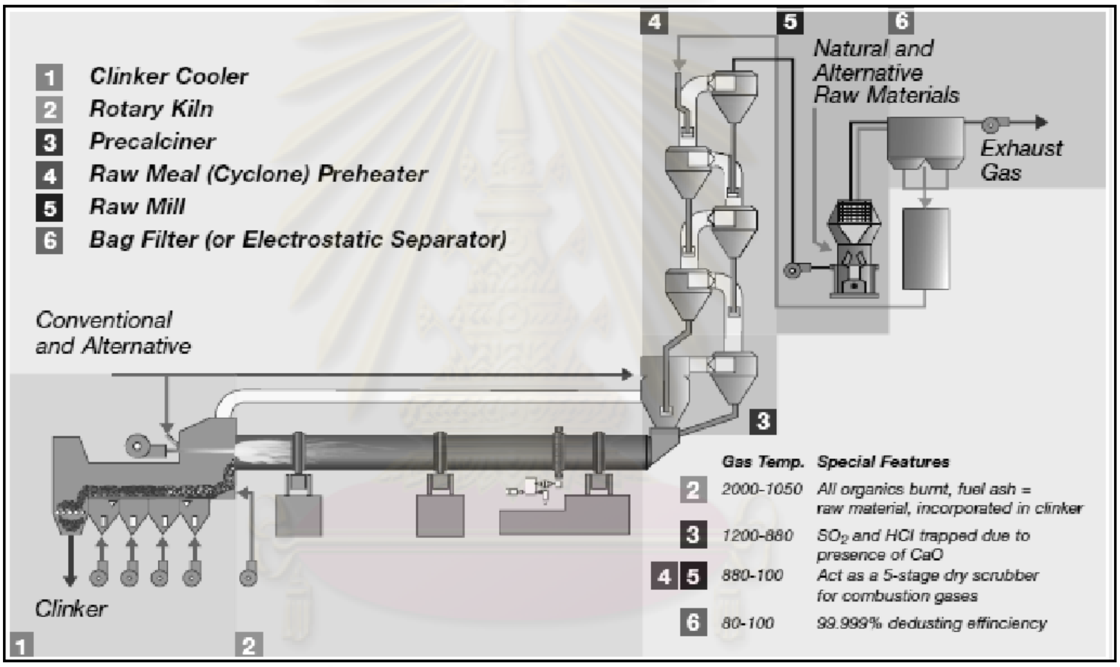


Figure 2.11 The utilizations of AFR in cement production (Holcim and GTZ, 2006)

The main objective of the permission and controlling process is to assure that only suitable wastes will be used and the AFR operations run properly. Regulators and kiln operators should be able to track the progress of the waste through the waste treatment path, either directly from a waste generator or through collecting/pre-treatment companies. The quality of the material designated for co-processing is crucial. Quality data and emissions monitoring data form the basis for scientific discussions with external stakeholders. They are also helpful tools for reducing local concern and the notion that cement plants are misused as trash bins for uncontrolled disposal of wastes. Co-processing should only be applied if not just one but all tangible pre-conditions and requirements of environmental, health and safety, socio-economic and operational criteria are fulfilled. As a consequence, not all waste materials are suitable for co-processing. Table 2.9 gives an overview for the justification of waste not being recommended for co-processing in cement plants. Cement plant operators must know the quantity and characteristics of the available wastes before applying for a permit for co-processing. However, an open communication channel and regular consultations between the public and the private sector will help to reduce possible friction and misunderstandings and to develop a permit process most suitable for all involved

Table 2.9 List of waste material not suited for co-processing and the main reasons for the exclusion from co-processing (Holcim and GTZ, 2006).

List of waste material	Enrichment of pollutants in the clinker	Emission values	OH&S	Potential for recycling	Landfilling	Negative impact on kiln operation
Electronic waste	X	X		X		
Entire Batteries	X	X		X		X
Infectious & medical waste			X			
Mineral acids and corrosives		X	X			X
Explosives	X		X			X
Asbestos			X		X	
Radioactive waste	X		X			
Unsorted municipal waste	X	X		X		X

The utilization of hazardous and industrial waste as AFR depends on the amount of silicates, calcium, and alumina, which are the basic constituents of cement. To emphasize the potential of utilization waste as AFR, Table 2.10 showed some examples of hazardous and industrial waste information and Table 2.11 summarized alternative fuel options for the cement industry. Table 2.12 was given type of heavy metals in alternative raw materials and fuel. The replacement by waste should be done with very restricted amount because too much addition of wastes may be negative affect some physical and chemical properties of Portland cement. For example, heavy metals may deteriorate some important properties of cement.

Table 2.10 Examples of Hazardous Industrial Wastes in Portland cement Production

Industrial Waste	Favorable composition (% by weight)	Highest % Addition possible	Reference
Ash from pyrolysis of used oil from car	21.34% CaO; 3.80%SiO_2; 1.64% Al_2O_3; and 2.32% Fe_2O_3	-	Tezza and Scian, 2000
Galvanic sludge from electroplating	43.19% Ca; 9.02% Si ; 2.33% Al; and 1.88% Fe	2%	Ract, Espinosa, Tenorio, 2003
Municipal solid waste incineration (MSWI) ash	27.02% CaO; 29.4%SiO_2; 18.0% Al_2O_3; and 13.3% Fe_2O_3	< 5%	Shin et al., 2003
Industrial Borax Wastes (BW) from production of borax from tincal.	13.97%CaO; 18.24% SiO2; 2.05% Al2O3; and1.04%Fe2O3	-	Elbeyl,2004

Table 2.11 Alternative fuel options for the cement industry (U. Kääntee et al.2004)

Type of Alternative fuel	**Example of alternative fuel**
Liquid waste fuels	Tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste, oil sludge
Solid waste fuels	Petroleum coke (‘‘pet coke’’), paper waste, rubber residues, pulp sludge, used tires, battery cases, plastic residues, wood waste, domestic refuse, rice chaff, refuse derived fuel, nut shells, oil-bearing soils, sewage sludge
Gaseous waste	Landfill gas, pyrolysis gas

Table 2.12 Heavy metals in Waste and fuels in Portland cement (Achterbosch el.at. 2003)

Metals	Secondary fuel	Secondary raw material
As	NA	Coal fly ash, wastes from iron and steel industry
Cd	Used tires, fractions of municipal, commercial, and industrial wastes	Wastes from iron and steel industry
Co	Used tries	Wastes from iron and steel industry, iron ore, fly ash and foundary sand
Cr	Used tries	Wastes from iron and steel industry, iron ore, ashes from burning process
Cu	Fractions of municipal, commercial, and industrial wastes	Coal fly ash, waste from iron and steel industry
Ni	ND	Coal fly ash, waste from iron and steel industry
Pb	Used tries, waste oil	Coal fly ash, waste from iron and steel industry, iron ore
Sn	ND	Waste from iron and steel industry
V	ND	Coal fly ash
Zn	Used tries, waste oil	Waste from iron and steel industry, iron ore

NA: Non-Available

2.8 Iron industry and grinding sludge

The iron and steel industry is the main basic industry in Thailand. This industry is the primary industry to support other industry such as computer and electronic, automobile parts, construction, food container and packaging, and furniture. The demand of iron and steel in country is approximately 13 tons per year and it still increase.

The iron and steel industry consists of iron making, steel making, casting, primary forming, and secondary forming. The iron making is the smelting iron ore by mixing charcoal and lime, burning into blast furnace and receiving hot metal or liquid pig iron. When iron is smelted, the hot metal contains more carbon than is desirable. To become steel, it must be melted and reprocessed to reduce the carbon to the correct amount, at which point other elements can be added. This liquid is then continuously cast into long slabs or cast into ingots in primary forming process. Finally, the ingots are sent into secondary forming for producing slabs, blooms, or billets. Slabs are hot or cold rolled into sheet metal or plates. Billets are hot or cold rolled into bars, rods, and wire. Blooms are hot or cold rolled into structural steel, such as I-beams and rails. Overall of iron and steel industry was show in Figure 2.11 and 2.12.

Grind sludge is a residue from manufacturing, fabrication and finishing for other industry. The grinding sludge can produce from shaping, machining, and joining process. Iron forging is one of the industries, which produce the grinding sludge as waste. Some production process of iron forging was illustrated in Figure 2.13.

Grinding sludge, one of the main hazardous wastes produced by the iron forging industry, is classified as a hazardous waste under Thailand regulations by the Department of Industrial Works, under the Ministry of Industry (DIW, 2006). Its main components are heavy metals such as iron, chromium, cadmium, nickel, and zinc. The general treatment of grinding sludge is its disposal in a secure landfill; however, this sludge has potential uses as a substitute iron ore in raw material preparations.

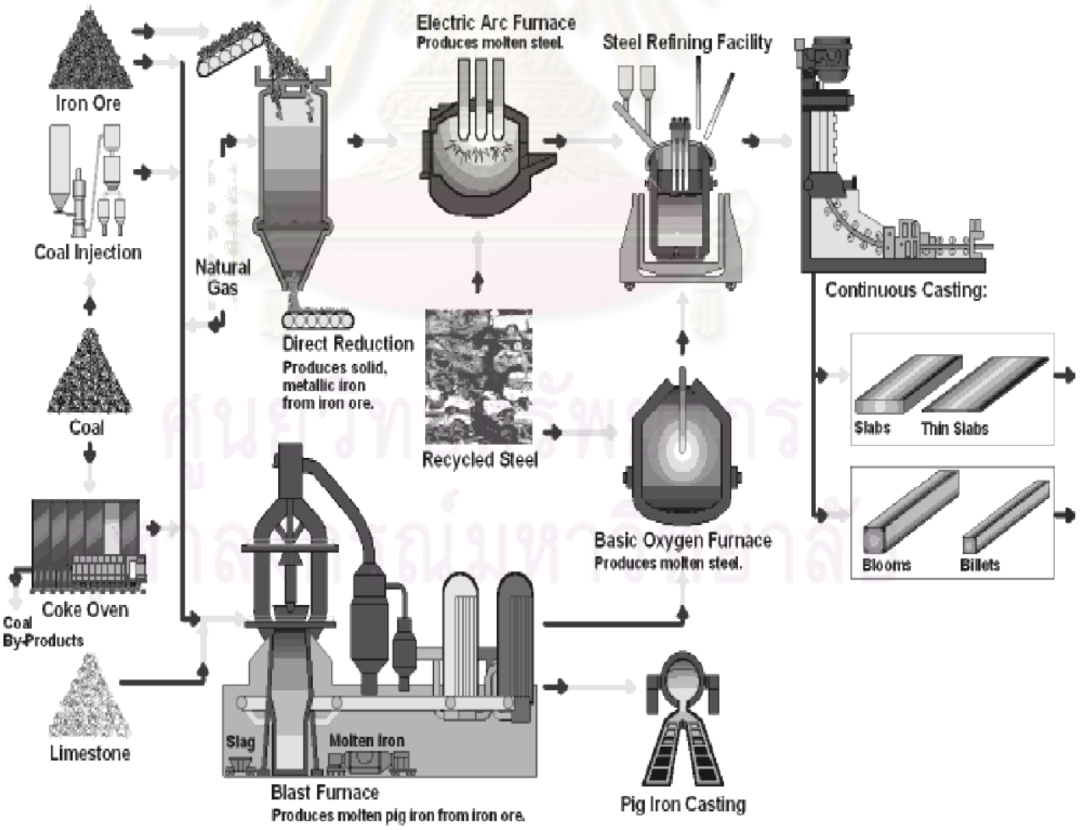


Figure 2.12 Iron making process and steel making process

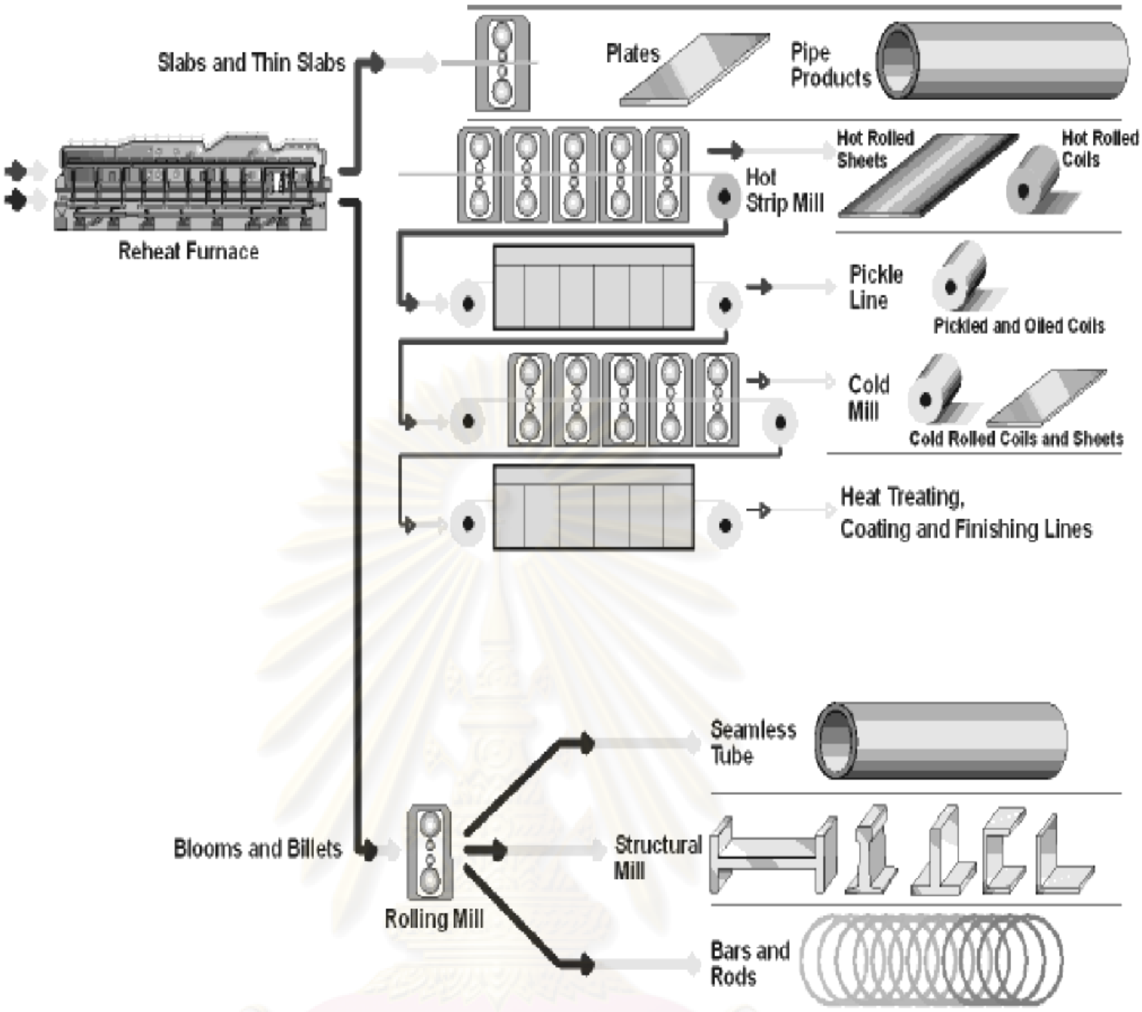


Figure 2.13 Primary and secondary forming processes

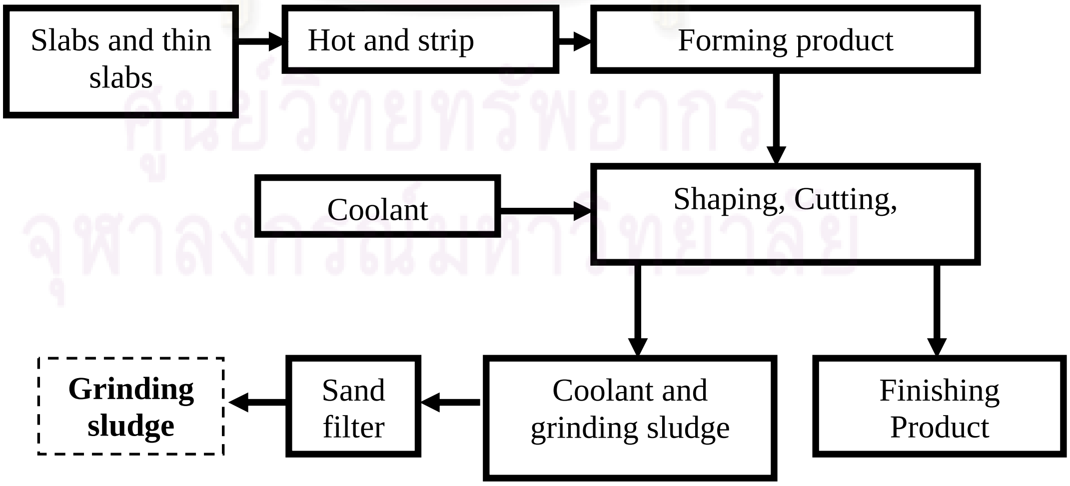


Figure 2.14 Iron forging industry and grinding sludge

2.9 Heavy metal

A heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term of heavy metal has been called "meaningless and misleading" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis". There is an alternative term toxic metal, for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals. One source defines heavy metal as one of the "common transition metals, such as copper, lead, and zinc. These metals are a cause of environmental pollution (heavy-metal pollution) from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain." Another common definition is based on the density of the metal (hence the name heavy metal), classifying all metals weighing more than 5000 kg/m3, such as lead, zinc and copper, as heavy metals. Heavy metals occur naturally in the ecosystem with large variations in concentration. Nowadays anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Waste derived fuels are especially prone to contain heavy metals so they should be a central concern in a consideration of their use.

Living organism require varying amount of heavy metals such as iron, cobalt, copper, manganese, molybdenum, and zinc. Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten, and even cadmium. The general properties, source, usefulness in manufacturing, adverse effect and some limitation standards of some heavy metals were given in Table 2.13, Table 2.14, Table 2.15 and Table 2.16, respectively.

Table 2.13 Properties of heavy metals

Heavy Metals	Atomic weight (g/mol)	Atomic Number	Color	Crystal structure	Element category	Chemical group	Melting point	Boiling point	Density at 293 K (g/cm^3)	Oxidation states
Aluminum (Al)	26.981	13	grey	Face-centered cubic	Poor Metal	IIB	933.47 K 660.32 °C	2792 K 2519 °C	2.70	3
Calcium (Ca)	40.078	20	Silver, Dull grey	Face-centered cubic	Alkaline earth metal	IIA	1115 K 842 °C	1757 K 1484 ° C	1.55	2
Cadmium (Cd)	112.411	48	silvery gray metallic	hexagonal	Transition metals	IIIB	594.22 K 321.07 °C	1040 K 767 °C	8.65	2, 1
Chromium (Cr)	51.995	24	silvery metallic	body-Centered cubic	Transition metals	VIA	2180 K 1907 °C	2944 K 2671 °C	7.19	6, 5, 4, 3, 2, 1, -1, -2
Copper (Cu)	63.546	29	reddish/orange metallic luster	face-centered cubic	Transition metals	IB	1357.77 K 1084.62 °C	2835 K 2562 °C	8.94	+1, **+2**, +3, +4
Iron (Fe)	55.845	26	lustrous metallic with a grayish tinge	NA	Transition metals	VIIIA	1811 K 1538 °C	3134 K 2862 °C	7.87	2, 3
Potassium (K)	39.098	19	silvery white	body-centered cubic	Alkali metal	IA	336.53 K 63.38 °C	1032 K 759 °C	0.89	1
Lithium(Li)	3	6.911	silvery white in oil	body-centered cubic	Alkali metal	IA	453.69 K 180.54 °C	1615 K 1342 °C	0.53	+1, -1
Magnesium (Mg)	12	24.305	silvery white solid	hexagonal	Alkaline earth metal	IA	923 K 650 °C	1363 K 1091 °C	1.74	2
Manganese (Mn)	25	54.938	silvery metallic	cubic	Transition metals	VIIA	1519 K, 1246 °C,	2334 K, 2061 °C	7.21	7, 6, 5, 4, 3, 2, 1, -1, -2, -3
Sodium (Na)	11	22.989	silvery white metallic	body-centered cubic	Alkali metal	IA	370.87 K 97.72 °C	1156 K 883 °C	0.968	+1, -1
Nickel (Ni)	28	59.693	lustrous, metallic and silvery with a gold tinge	face-centered cubic	Transition metals	VII B	1728 K, 1453 °C	3186 K, 2732 °C	9.91	4, 3, **2**, 1, -1
Lead (Pb)	82	207.2	bluish gray	Face centered cubic	Transition metals	IVB	600.61 K 327.46 °C	2022 K 1749 °C	11.34	4, **2**, -4
Vanadium (V)	23	50.941	blue-silver-grey metal	body-centered cubic	Transition metals	VA	2183 K, 1910 °C	3680 K, 3407 °C	6.0	**5**, 4, 3, 2, 1, -1
Zinc (Zn)	30	65.39	bluish pale gray	hexagonal	Transition metals	IIIB	692.68 K, 419.53 °C	1180 K, 907 °C	7.14	

Table 2.14 Sources of heavy metals and Usefulness in manufacturing (ATSDR)

Heavy Metals	Nature resource	Useful in manufacturing
Aluminum (Al)	Earth's crust, Bauxite ore	Beverage cans, Pots, Pans, Airplanes, Siding and roofing, Foil Antacids, Astringents, Food additives, Antiperspirants, Explosives, Fireworks, Alums in wastewater treatment
Calcium (Ca)	Calcium occurs in sedimentary rocks in the minerals calcite, dolomite and gypsum.	Some uses are as a reducing agent in the extraction of other metals, such as uranium, zirconium, and thorium, a deoxidizer, desulfurizer, or decarbonizes for various ferrous and nonferrous alloys, an alloying agent used in the production of aluminum, beryllium, copper, lead, and magnesium alloys, in the making of cements and mortars to be used in construction, in the making of cheese, where calcium ions influence the activity of rennin in bringing about the coagulation of milk.
Cadmium (Cd)	Earth's crust	Most cadmium used in the United States is extracted as a byproduct during the production of other metals such as zinc, lead, or copper. Cadmium is also recovered from used batteries.
Chromium (Cr)	Rocks, animals, plants, and soil.	Chromium is widely used in manufacturing processes. Chromium can be found in many consumer products such as: wood treated with copper dichromate, leather tanned with chromic sulfate, stainless steel cookware.
Copper (Cu)	Earth's crust, rock, soil, water, sediment	Metallic copper is most commonly used I electrical wiring, and some water pipes. It is also found in many mixtures of metals, called alloys, such as brass and bronze. The most commonly used compound of copper is copper sulfate.
Iron (Fe)	Earth's crust	Iron is the most widely used of all the metals, accounting for 95% of worldwide metal production. Its low cost and high strength make it indispensable in engineering applications such as the construction of machinery and machine tools, automobiles, the hulls of large ships, and structural components for buildings.
Manganese (Mn)	Rocks and soil.	Manganese is used principally in steel production to improve hardness, stiffness, and strength. Manganese is also used in a wide variety of other products, including: fireworks, dry-cell batteries, fertilizer, paints, a medical imaging agent, cosmetics. It may also be used as an additive in gasoline to improve the octane rating of the gas. Small amounts of manganese are used in a pharmaceutical product called mangafodipir trisodium (MnDPDP) to improve lesion detection in magnetic resonance imaging of body organs.
Nickel (Ni)	Earth's crust, sea floor nodule	Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc. These alloys are used in making metal coins and jewelry and in industry for making items such as valves and heat exchangers. Nickel compounds are used for nickel plating, to color ceramics, to make some batteries, and as substances known as catalysts that increase the rate of chemical reaction
Lead (Pb)	Earth's crust	Lead is used in building construction, lead-acid batteries, bullets and shot, weights, and is part of solder, pewter, fusible alloys and radiation shields
Zinc (Zn)	Earth's crust	Zinc has many commercial uses as coatings to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass, and bronze. Zinc compounds are widely used in industry to make paint, rubber, dyes, wood preservatives, and ointments

Table 2.15 Adverse effect of heavy metals (ATSDR)

Heavy Metals	Chronic exposure	Acute exposure
Aluminum (Al)	Some studies show that people exposed to high levels of aluminum may develop Alzheimer's disease. Rats and hamsters showed signs of lung damage after breathing very large amounts of aluminum as chlorohydrate.	Factory workers who breathe large amounts of aluminum dusts can have lung problems, such as coughing or changes. People may get skin rashes from the aluminum compounds in some underarm antiperspirants.
Cadmium (Cd)	Eating lower levels of cadmium over a long period of time can lead to a build-up of cadmium in the kidneys. If the levels reach a high enough level, the cadmium in the kidney will cause kidney damage. Cadmium compounds are known human carcinogens	Eating food or drinking water with very high cadmium levels severely irritates the stomach, leading to vomiting and diarrhea, and sometimes death.
Chromium (Cr)	The main health problems seen in animals following ingestion of chromium (VI) compounds are to the stomach and small intestine (irritation and ulcer) and the blood (anemia). System sperm damage and damage to the male reproductive system. Chromium (VI) compounds as known to be human carcinogens.	These health effects include irritation of the lining of the nose, runny nose, and breathing problems (asthma, cough, shortness of breath, wheezing).
Copper (Cu)	Long term exposure to copper dust can irritate your nose, mouth, and eyes, and cause headaches, dizziness, nausea, and diarrhea.	If you drink water that contains higher than normal levels of copper, you may experience nausea, vomiting, stomach cramps, or diarrhea. Intentionally high intakes of copper can cause liver and kidney damage and even death.
Manganese (Mn)	Sperm damage and adverse changes in male reproductive performance were observed in laboratory animals fed high levels of manganese.	Nervous system disturbances have been observed in animals after very high oral doses of manganese, including changes in behavior. Illnesses involving the kidneys and urinary tract have been observed in laboratory rats fed very high levels of manganese. These illnesses included inflammation of the kidneys and kidney stone formation
Nickel (Ni)	The EPA has determined those nickel refinery dust and nickel subsulfides are human carcinogens. The most serious harmful health effects from exposure to nickel, such as chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus. Eating or drinking levels of nickel much greater than the levels normally found in food and water have been reported to produce lung disease in dogs and rats and to affect the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development.	The most common harmful health effect of nickel in humans is an allergic reaction. The most common reaction is a skin rash at the site of contact. Workers who accidentally drank light green water containing 250 ppm of nickel from a contaminated drinking fountain had stomach aches and suffered adverse effects in their blood (increased red blood cells) and kidneys (increased protein in the urine).
Lead (Pb)	Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. The Department of Health and Human Services (DHHS) has determined that lead and lead compounds are reasonably anticipated to be human carcinogens and the EPA has determined that lead is a probable human carcinogen.	The main target for lead toxicity is the nervous system, both in adults and children. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High level exposure in men can damage the organs responsible for sperm production
Zinc (Zn)	Putting low levels of zinc acetate and zinc chloride on the skin of rabbits, guinea pigs, and mice caused skin irritation. Skin irritation will probably occur in people	Harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting. Inhaling large amounts of zinc (as dusts or fumes) can cause a specific short-term disease called metal fume fever.

Table 2.16 Some of environmental standards

Heavy Metal	Environmental Standard				
	Drinking water standard, mg/L (PCD)	Surface Water standard Type III, mg/L (PCD)	Industrial effluent standard, mg/L (DIW)	STLC Standard, mg/L (DIW)	TCLP standard US EPA
pH	6.5-8.5	5-9	5.5-9.0	≤ 2 or ≥ 12.5l	≤ 2 or ≥ 12.5l
Aluminum (Al)	NA	NA	NA	NA	NA
Calcium (Ca)	75-200	NA	NA	NA	NA
Cadmium (Cd)	< 0.01	NA	<0.03	1.0	1.0
Chromium (Cr^{+6})	< 0.05	0.005^{*} 0.05^{**}	<0.25	5	5.0
Chromium (Cr^{+3})	NA	NA	<0.75	5	5.0
Copper (Cu)	1.0-1.5	< 0.1	<2.0	25	NA
Iron (Fe)	0.5-1.0	NA	NA	NA	NA
Potassium (K)	NA	NA	NA	NA	NA
Lithium(Li)	NA	NA	NA	NA	NA
Magnesium (Mg)	50-150	NA	NA	NA	NA
Manganese (Mn)	0.3-0.5	< 1.0	< 5.0	NA	NA
Sodium (Na)	NA	NA	NA	NA	NA
Nickel (Ni)	NA	< 0.1	< 1.0	20	NA
Lead (Pb)	< 0.05	< 0.05	< 0.2	5.0	5.0
Vanadium (V)	NA	NA	NA	24	NA
Zinc (Zn)	5.0-15	< 1.0	< 5.0	250	NA

2.10 Heavy metals in cement

When a cement kiln burns hazardous and other wastes or incorporates waste into its raw meal mix, residues from these wastes are inevitably incorporated into the clinker and, thus, the cement. The residues of primary concern are heavy metals. It is surprising that scientists and engineers concerned with the properties of cements and concretes have not intensively studied the effects on hazardous waste of cement kilns.

In 1993, Kleppinger pointed out the potential environmental problems on co-processing of hazardous waste in cement kin. These issues related on fate of heavy metals in clinker and cement kiln dust, the limitation of heavy metal contain in cement product, types of hazardous waste fed to kilns, and effect of residues after burning hazardous waste on properties of cement product. Moreover, Sprung (1985) suggested that the properties of Portland cement are decisively influenced by the composition as well as the by the thermal and mechanical treatment of the clinker. The clinker composition depends in the first instance on the chemical and mineralogical nature of the raw material mix. It can also be modified by the fuel type and its components. Depending upon the type of preprocessing employed, material circulations in the kilns and pre-heater often lead to concentration or reduction of the easily volatile substances (metals and inorganic salts) and thus modify the composition of the clinker.

The literature review of heavy metals in cement related to the effect of heavy metals on physical, chemical, and engineering properties in cement product. For example, the cement phase in cement was considered on the decomposition of increment of C_3S, C_2S, C_3A, and C_4AF. Moreover, the engineering properties were setting time, compressive strength, and grinding ability. Finally, the physical properties were the observation texture and product color. Table 2.17 was explained on effects of heavy metals on cement manufacture and properties. Table 2.18 was given the concentration of heavy metals in the raw mixtures and clinker and environmental materials. Table 2.19 and Table 2.20 were illustrated the effects of heavy metals on cement properties. Finally, Table 2.21 was concluded the utilization waste as alternative fuel and raw materials as AFR in cement production.

Table 2.17 Effects of heavy metals on cement manufacture and properties (Dalton, el at., 2004)

Heavy metals	**Effect on cement manufacture and properties**
As	Typical enters clinker; unlikely to affect cement manufacture
Cd	Cd concentration in clinker decreased as Chloride input to kiln increases. High Cadmium oxide content in clinker retarded hydration but it still occurred normal strength.
Cr	Cr reduced viscosity of clinker melt. It incorporated into clinker phases, accelerated hydration reaction, improved early strength.
Cu	Cu accumulated in clinker.
Pb	It can volatile, may exit the kiln as fines and collect in CKD. It can accumulate in clinker without adverse effect if the concentration of lead was less than 70 ppm.
Hg	It is highly volatile, expected to escape in stack gases and little effect on clinker production.
Zn	The incorporation degree of zinc in clinker is 80-90% and the rest is into cement kiln dust.

Table 2.18 Concentration of heavy metals in the raw mixtures and clinker (cite in Stephan and el at., 1999)

Heavy metals	**Crust of the earth**		**Soil world wide**	**Raw mix**					**Clinker**										
				HMB			**VDZ**		**HMB**			**VDZ**		**UK**			**USA**		
	Min.	**Max.**	**Avg.**	**Min**	**Max**	**Avg.**	**Min**	**Max**	**Min**	**Max**	**Avg.**	**Min**	**Max**	**Min**	**Max**	**Avg.**	**Min**	**Max**	**Avg.**
As	1	13	5	3	28	11	3	15	2	87	15	2	15	10	160	43	5	71	19
Cd	0.03	0.3	0.5	0.04	1.0	0.2	0.04	0.15	0.01	1.5	0.2	0.01	1.5	<0.1	1.0	0.4	0.03	1.12	0.34
Cr	4	2980	200	23	39	27	23	34	11	319	30	10	90	51	96	70	23	422	76
Cu	4	87	NA	NA	NA	17	NA	NA	5	136	40	NA	NA	16	192	44	NA	NA	NA
Hg	0.004	0.4	0.08	0.02	0.6	0.07	NA	NA	<0.02	1.2	0.2	<0.01	NA	NA	NA	NA	<0.001	0.036	0.014
Ni	2	2000	40	18	30	22	18	23	12	397	30	10	50	NA	NA	NA	10	129	31
Pb	1	20	10	4	23	12	4	15	1	105	25	5	105	0.5	88	15	1	75	12
Tl	0.1	0.5	NA	0.1	6.0	0.5	0.21	0.78	0.01	1.2	0.2	<0.01	NA	0.04	0.48	0.28	0.01	2.68	1.08
V	NA	NA	100	32	102	50	NA	NA	10	100	30	20	100	15	111	56	NA	NA	NA
Zn	16	130	50	15	90	30	31	47	29	537	60	40	350	28	198	96	NA	NA	NA

NA: Non Available

Table 2.19 Effect of Heavy metals on chemical properties in cement product

Heavy metals	Incorporation degree in clinker,% (by Weight)	Cement product properties: Chemical Properties					Referance
		Free lime	C_3S -belite	C_2S-alite	C_3A	C_4AF	
Cd	51(9),(14) 22(4)	Decrease(11)	Incorporate (4)	Incorporate (4)	NA	NA	(1) Kirchner, 1986 (2) Gerger, 1994 (3) Sprung and Rechenberg, 1994 (4) Murat and Sorrentino, 1996 (5) Kakili, Parissakis, and Bouras, 1996 (6) Stephan, Mallmann, Knofel, and Hardtl, 1999(a) (7) Stephen, Maleki, Knofel, and Hardtl, 1999 (a) (8) Stephen, Maleki, Knofel, and Hardtl, 1999 (b) (9) Espinosa and Tenorio, 2000 (10) Potgieter, el.at., 2002 (11) Kolovos,Tsivlis and kakali,2002 (12) Ract, Espinosa and Tenorio, 2003 (13)Andrade,Maringolo, and Kihara, 2003 (14) Barros, Tenorio, and Espinosa, 2004
Cr	99(11); 84(4)	Increase (6), (7),(11)	Incorporate (4) Increase (6),(7)	Incorporate (4) Decrease (6),(7)	NA	NA	
Cu	99.3(11),(12)	Decrease(5)	Incorporate (5),(11) Increase (5),(11)	NA	NA	NA	
Mn	NA	Increase(11)	NA	Incorporate (11) Increase (11)	NA	Incorporate (11)	
Ni	97(9); 100(12)	Decrease(6)	NA	NA	NA	NA	
Pb	37.1(13); 25(3); 97(2); 54(3),(14),100(1) ;0(4)	NA	Incorporate (4)	NA	Incorporate (4)	NA	
Ti	NA	Decrease(10)	Incorporate (10) Increase (10)	Incorporate (10) Decrease (10)	NA	NA	
V	69.6(13)	Decrease(11)	NA	Incorporate (11) Increase size (11),(13)	NA	NA	
Zn	86(13); 75(9),(14) ;53(4)	Decrease(6)	Incorporate (4)	Incorporate (4) Decrease (6)	Incorporate (4) Decrease (6)	Incorporate (4)	

NA: Non- available

Table 2.20 Effect of heavy metals on cement properties in cement product

Heavy metals	Cement product properties: Physical properties				Other	Reference
	Color Texture & Structure	Clinker Grinding Ability	Setting Time	Compressive Strength		
Cd	NA	NA	Inhibit (2)	Reduce(2)	Cd immobilized by physical entrapment of Cd(OH) into the CSH and can delay in the formation of C_3AH_6 hydrated phase. (2)	(1) Kakali, and Parissakis, 1994 (2)Murat and Sorrentino, 1996 (3)Tsivillis and Kakali,1997 (4) Stephan, Mallmann, Knofel, and Hardtl, 1999(a) (5) Stephan, Mallmann, Knofel, and Hardtl, 1999(b) (6) Stephen, Maleki, Knofel, and Hardtl, 1999 (a) (7) Stephen, Maleki, Knofel, and Hardtl, 1999 (b) (8) Espinosa and Tenorio, 2000 (9) Barros, Tenorio, and Espinosa,2002 (10) Kakili, Parissakis, and Bouras, 1996 (11) Potgieter, el.at., 2002 (12) Kolovos,Tsivlis and kakali,2002
Cr	NA	High(3)	Rapid (2), (5)	Increase early strength (2)	Cr increased early strength but deteriorates at 28 day strength.(2) Cr is preferentially found in the silicate phase, especially in C_2S and formed K2Cr2O7 when K is high enough in clinker. (4) Cr retarded the heat liberation and prevents the hydration of C_4AF.(7) Cr_2O_3 can incorporate into clinker.(9)	
Cu	Dark (12)	Moderate(3)	NA	NA	The addition of CuO affects the formation of silicates as well as the formation of aluminates.(10)	
Co	NA	Moderate(3)	NA	NA	NA	
Mn	NA	High(3)	NA	NA	NA	
Mo	NA	Low-moderate(2)	NA	NA	NA	
Ni	NA	Moderate(3)	Normal (5)	NA	Ni was found in the clinker phase, mainly in the hexagonal shape. (4) NiO can incorporate into clinker.(9)	
Pb	NA	NA	Delay (2)	NA	The incorporation of Pb depended on chemical salt form and the small amount in clinker can reduce the effect of hydration and fixiation.(2)	
Ti	NA	Low-moderate(3)		Decrease early strength (2)	NA	
V	NA	Low-moderate(3)	NA	NA	V decreased the melt viscosity, favours the formation of big C_2S.	
Zn	Brown(1)	Low(3)	Retard(2)	Reduce(2)	C3S size crystals incrassated with the ZnO addition. (2) Zn is found in the aluminate and ferrite. (4) Zn retarded the heat liberation. (6),(7)	

NA: Non- available

Table 2.21 Utilization waste as alternative fuel and raw materials as AFR in cement production

Waste	Source	Element	Results	Reference
Galvanic sludge	Electroplating	Cr	Galvanic sludge additions of to 2.0 %wt in the cement raw meal does not affect clinkerization and consequently the clinkerization process.	Espinosa and Tenorio, 2000
Ashes from pyrolysis	Used oil car	Pb, Zn	The addition ash decreased the energy for milling, showed the low porosity.	Trezza, and Scian, 2000
Phosphogysum and oil shale	Fertilizer plants	$CaSO_4$	The intensity and the amount of belite peak were increasing burning temperature.	Öztürk,Suyadal, and Oguz,2000
MSW ash	Incinerator	NA	50% of raw materials for cement production can be obtained from incineration ash of MSW.	Kikuchi, 2000
Stibnite ore	Mining	Sb, S	The addition of the mineral containing Sb promoted the consumption of free lime and improved the burnability of clinker. Sb slightly retarded hydration reaction but helped to improve strength.	Kakali, el.at., 2003 Kakali, el.at., 2005
Galvanic sludge	Electroplating	Cu, Ni	The addition of galvanic sludge containing 2.4% wt and 1.2% Ni did not affect the clinkerization reaction. It decreased the reaction temperature of C2S and of liquid formation.	Ract, Espinosa and Tenorio, 2003
Contaminated sediments	Harbors and waterways	Ca, Si, Cl	The kiln operational conditions may have to be adjusted depending upon the quartz content of the sediments. High chloride content in this waste did not increase the effects in clinker.	Jennifer, el at., 2004
Borax Waste	Borax industry	B	The high boron level caused a decrease in compressive strength and increased the soundness expansion in PC.	Elbeyli,2004
Stibnite ore	Mining	W, Sb, S	The added mineral improved the burnability of cement raw mixture without affecting significantly the hydration rate and the cement properties.	Kakali, el at., 2005
Chemical precipitation Sludge	Surface finishing and electroplating industry	Ni, Cu, Pb, Cr	The large amount of sludge can inhibite C_3S in clinker. The leaching results shown that the trapped elements in hydrated samples would not leach out under acidic conditions. These wastes have the potentials to be utilized as alternative raw materials in cement production.	Shin, Chang, Lu, and Chiang, 2005
Tire derived fuel (TDF)	Car	Zn, Cr	The amount of Zn and Cr fron thuse TDF are not problem to clinker.	Pipilikaki, el at.,2005

Table 2.21 Utilization waste as alternative fuel and raw materials as AFR in cement production (continue)

Waste	Source	Element	Results	Reference
Bullet alloy	Ammunition	Pb, Cu, Zn, Sn, Sb	The contents of lead measured in the modified clinkers show an average incorporation degree of 46%, a value that should be considered high, in comparison to relative published data. Almost all amounts of Cu, Zn, Sn and Sb in the modified raw mixes are retained in clinker. Except from Pb, which was preferentially found in the silicate phases, Cu, Zn, Sn and Sb are mainly concentrated in the melt, affecting the growth environment of alite crystals and modifying their shape and size.	Kolovos,2006
tanned leather shavings whit chrome salts	Tannery Industry	Cr^{3+}	The addition of leather shavings containing chrome in the raw materials used in the production of Portland cement clinkers produce modifications in the crystalline characteristics of the main phases of the clinker. The hydration study of the clinkers obtained with the addition of shavings with chrome showed an acceleration of the initial hydration speed (first 48 hours) affecting the beginning and the end of the setting time.	Trezza, and Scian, 2007
Steel slag	Scrap smelting in arc furnace	Fe	The alite phase as small well formed crystals. The belite crystal were distributed in relation to alite, indicating that the clinker reaction had proceeded extensively in the direction of alite and that raw mix was homogenous. The liquid phase occurred as fine crystals, uniformly distribution. The steel slag can be used as raw materials in cement production.	Tsakiridis,Papadimitriou, tsivilis, and Koronros, 2008
Copper slag	Smelting and refining of copper	Cu	Copper slag has a high Fe content and has been used as an iron adjustment material during the cement clinker production. The cement product produced by using copper slag performed even better than using iron powder. The use of copper slag also results in lower required calcination temperature and improved grindability of the clinker although the raw materials cost may or may not be reduced depending on the local availability of copper slag.	Shi, Meyer, and Behnood, 2008
Electroplating sludge	Electroplating industrial and automobile components	Ni, Zn, Cu, Cr	The nickel, zinc, and chromium have positive effects on C_2S stabilization ($Cr^{3+} > Ni^{2+} > Zn^{2+}$), whereas copper has a negative effect. The addition of up to 10% electroplating sludge did not have any negative influence on the formation of C_2S. It was observed that C_2S decreased while C_2S increased with a rise in the addition of the electroplating sludge. Moreover, nickel and chromium mainly contributed to stabilizing C_2S in the belite-rich clinkers produced from the electroplating sludge.	Chen, el. at. 2009

CHAPTER III

METHODOLOGY

This study was divided into three parts: raw material analysis, distribution of heavy metals in Portland cement clinker and leaching behavior of heavy metals on cement product. The overview of all methodology was shown in Figure 3.1, Figure 3.2 and Figure 3.3.

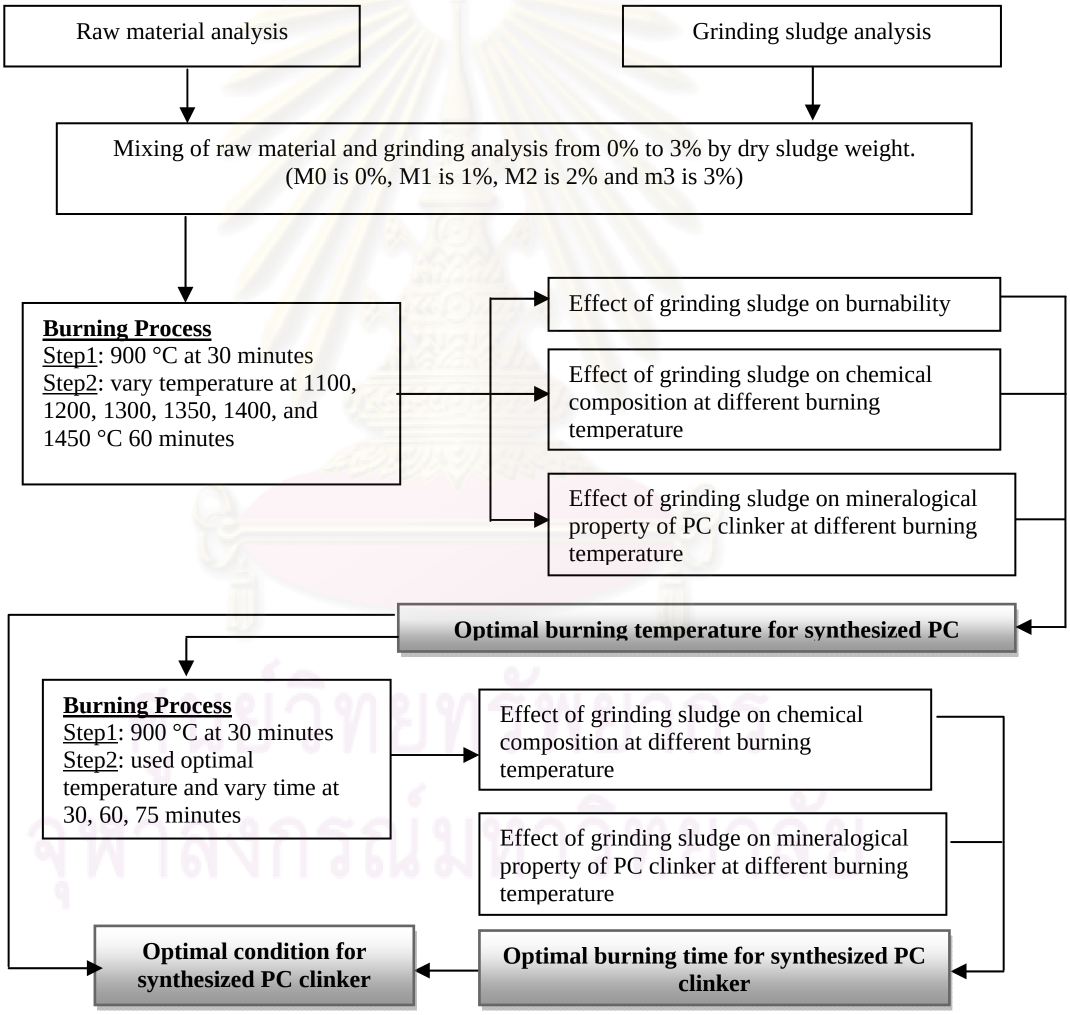


Figure 3.1 Overview of methodology 1

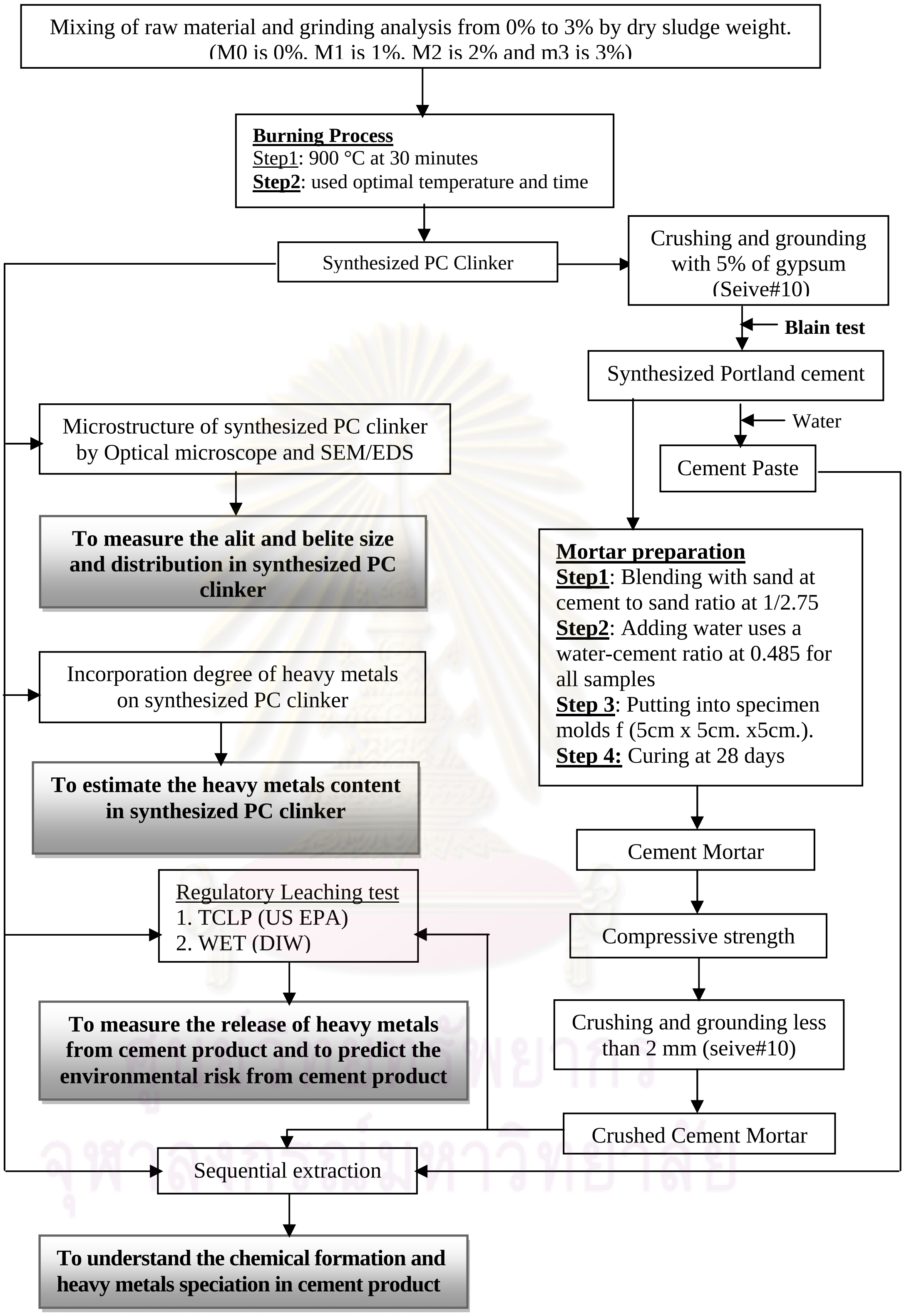


Figure 3.2 Overview of methodology 2

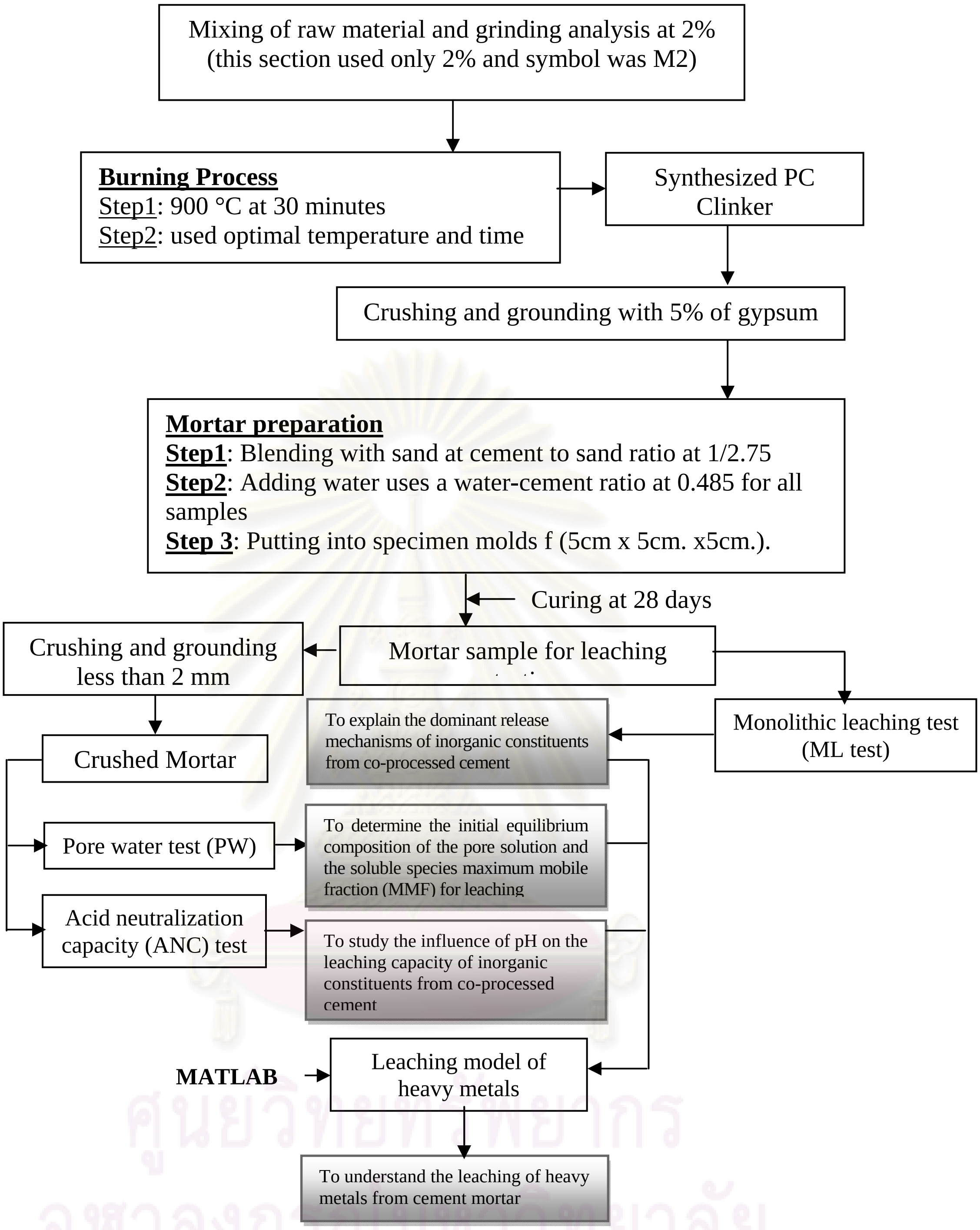


Figure 3.3 Overview of methodology 3

3.1 Materials

3.1.1 Raw meal

The raw material or raw meal was collected from Siam City Cement Public Company and homogenized to obtain particle sizes of less than 125 µm (through 120-mesh sieve). The raw meal consists of limestone, shale mix, shale core, and iron ore. The chemical compositions of the raw mix were analyzed by X-ray fluorescence spectroscopy.

3.1.2 Grinding sludge

Grinding sludge from the iron forging industry was received from a waste collector. It was dried at 105°C for 24 hours in a laboratory electrical oven. The analysis of grinding sludge was done according to procedures set by Siam City Cement PCL-owned alternative fuel and raw materials laboratory and total heavy metal analysis were done using microwave digestion and inductively- coupled plasma spectroscopy. All of parameters were given on Table 3.1**.**

Table 3.1 Chemical and physical testing for grinding sludge

Parameters	**Method and Scientific instrument**
1. Heating Value	Bomb calorimeter
2. Heavy metals	Acid digestion by US EPA Method 3052 and Inductively couple plasma atomic emission spectroscopy (ICP-AES)
3. Chloride	Chloride Potentiometer titration (ASTM D-1522)
4. Sulfur	ASTM D-1266
5 Chemical composition	X- ray fluoresce spectroscopy (XRF)
6. pH	pH meter

3.1.3 Raw material preparation

1%, 2%, and 3% by weight of grinding sludge were mixed with cement raw meal. The above samples are referred as M1 – M3 respectively, while sample M0 is the sample with no addition of grinding sludge. Homogeneity was ascertained by dosing the added grinding sludge on the mixtures. The ratios of the mixtures were show in Table 3.2.

Table 3.2 Ratios of grinding sludge mixed with raw meal

Sample	Raw meal, %	Grinding sludge, %
M0	100	0
M1	99	1
M2	98	2
M3	97	3

3.2 Burning process

The burning process was used to finding the optimal conditions for synthesized Portland cement clinker. The optimal conditions consisted of burning temperature and time. There are two steps for burning including preheating and burning process.

Step 1: Burning for preheat raw mix at 900 °C 30 minutes

Step 2: Burning for formation of cement phase

The synthesized Portland cement (PC) clinker found the optimal burning temperature and time as optimal burning condition. This research was varied the burning temperature and time at step 2. The vary temperature began at 1100, 1200, 1300, 1350, 1400, and 1450 and was fix time at 60 minutes. The synthesized samples at different temperatures were analyzed clinker properties. The results were used to choose the desired temperature.

The desired temperature was used in step 2 for find optimal time. This research was varied time at 30, 60, and 75 minutes. The synthesized samples at different times were analyzed clinker properties. The results were used to choose the optimal time.

The optimal burning condition was use for synthesized PC clinker for all samples. The synthesized PC clinker samples were ground and mixed with 5% gypsum for producing cement. The cement samples were added water to prepare cement paste (using water/cement at 0.485). The cement mortars were produced by mixing of cement to sand ratio at 1:2.75, water to cement ratio at 0.485 for all samples. The curing days for cement mortar was 28 days. The unconfined compressive strength and blain test were tested by ASTM standard.

Figure 3.4 The synthesized Portland cement clinker

Figure 3.5 High temperature furnaces

3.3 Experimental Procedures

To clearly understand this work, the experimental procedures were separated into two parts as follow:

3.2.1 Distribution of heavy metals in co-processed PC clinker

3.2.2 Leaching of heavy metals form co-processed PC clinker and mortar

3.3.1 Distribution of heavy metals in co-processed Portland cement clinker

3.3.1.1 Effect of grinding sludge on burnability

The content of free lime in the clinker is a good parameter of the of burning process. The utilization of alternative raw materials and fuel in cement production has effect to cement properties. The free lime content is one of important cement properties. Hence it follows that a decrease in free lime means an improvement in the burnability by the addition of the metal in the specific concentration. In contrast a rise in the free lime means deterioration in the burnability. The content of free lime can also change when CaO takes place in a reaction that leads to a new compound.

The synthesized PC clinker at different temperature and time were found free lime content. Approximately 0.5 g. of sample was weight into flask which contained with 15 ml. of ethylene glycol and 7.5 ml. of methanol. This solution was boiled and equipped with reflux condenser. During boiling, the solution was mixed with stirrer for 30 minutes. After that, this solution was cooled by air. After cooling, the solution was filtrated by number 40 filter paper. Then, the obtained solution was added a few indicator. The indicator was 0.005 g. of methyl red and 0.5 g. of bromocresol green in 100 ml. methanols. The solution was titrated with 0.1 N HCl. An amount of free lime was calculated by equation 3.1:

$$\%\ \text{free lime} = \text{ml. of } 0.1\ N\ HCl \times 0.56 \qquad 3.1$$

The free lime results at different temperature were calculated the burnability by equation 3.2 and 3.3.

$$C = 2\,f\,CaO_{1100^\circ C} + 2\,f\,CaO_{1200^\circ C} + 3\,f\,CaO_{1300^\circ C} + 4\,f\,CaO_{1350^\circ C} + 4\,f\,CaO_{1400^\circ C} + 2\,f\,CaO_{1450^\circ C} \quad 3.2$$

$$\text{Burnability Capacity (BC)} = 600/C \quad 3.3$$

3.3.1.2 Effect of grinding sludge on chemical compound of PC clinker at different burning temperatures and time

The chemical composition of clinker is one of the main parameters. The main chemical compounds or cement phases contain tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). These chemical compounds were controlled by main oxide including calcium oxide (CaO), silica oxide (SiO_2), alumina oxide (Al_2O_3), and iron oxide (Fe_2O_3). The mixing of waste in raw materials or feeding waste as fuel can impact to qualitative and quantitative of PC clinker.

The modulus equation is used to control the proportion of main oxide in raw materials preparation process and the proportion of main oxide in PC clinker after burning process. The main modulus equations were the lime saturation factor (LSF), silica ration (SR), and alumina ration (AR).

The bogue equation is employed to roughly calculate the amount of main chemical compound as follow tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) in PC clinker.

The synthesized PC clinker at different temperature and time were determined the amount of main chemical oxide and minor oxide by X- ray fluorescence spectroscopy (XRF). The results were reported in percent of chemical oxide and were calculated in bogue and modulus equation.

Figure 3.6 X- ray fluorescence spectroscopy (XRF)

3.3.1.3 Effect of grinding sludge on mineralogical cement phase at different burning temperatures and time

This technique was used in order to identify the mineralogical phases formed during the sintering of the clinker and find out the differentiation caused by grinding sludge. The X-ray diffraction spectroscopy (XRD) is the scientific instrument to identify the crystalline compound in cement phases. The XRD pattern looks like a fingerprint of crystalline compound. The XRD result was commonly compared with the library standard or PDF profile.

The synthesized PC clinker at different temperature and time were crushed and blended until it looked like powder. The blended sample were filled and fixed in specimen mould. The parameter settings were explained in Table 3.3. The XRD results were compared with the cement company clinker from rotary klin.

Table 3.3 Setting parameter of XRD

Parameters	Settings
2θ	5-80 degree
Step size	0.1 degree.
Step time	1 second
Voltage	30 kV
Electric current	30 mA
Temperature	25°C

Figure 3.7 X-ray diffraction spectroscopy (XRD)

3.3.1.4 Microstructure of synthesized PC clinker by optical microscope (OM) and Scaning electron microscope with energy dispersive (SEM/EDS)

Microscopic examination of cement clinker has a long tradition, with optical microscopy, and more recently, scanning electron microscopy (SEM) making an invaluable contribution to Portland cement production. Microscopy of cement clinker (optical and SEM) is usually carried out on polished sections but thin sections can also be used.

a) Optical microscopy

Optical microscopy (OM), which is the light method, was used in order to study the effect of the added oxides on the texture of the produced clinker. The OM analysis explained the crystal size and distribution and other features of clinker to assess productions conditions such as raw material fineness, kiln temperature profile and cooling rate. The information obtained can then be used to predict the likely performance of cement made from the clinker, or perhaps indicate the cause of production difficulties such as poor combination.

The clinker sample were cracked and put in epoxy resin for polished section. A section of material that has been ground and plane polished on one face for examination, under a microscope, by reflected light. After that, the crystalline phase in sample was looked and taken photos at 5x, 10x, 50x and 100x.

Figure 3.8 Optical microscopy (OM)

b) Scanning electron microscope with energy dispersive spectroscopy (SEM/EDS)

SEM/EDS applied to cement clinkers opens up a completely new dimension of information unavailable by optical microscopy because X-ray microanalysis tells us the composition of the individual clinker minerals. Small changes in mineral composition can have a direct effect on clinkering and on hydration characteristics, so the clinker mineral compositions form a major part of a clinker assessment by SEM. Important physical parameters, such as crystal sizes, are also measured, just as they are using optical microscopy. Some information such as mineral color or birefringence cannot be assessed by SEM; the loss of color information is the price paid for the ability to quantify mineral compositions.

Figure 3.9 Scanning electron microscope with energy dispersive spectroscopy

3.3.1.5 Effects of heavy metals from grinding sludge on synthesized PC clinker

The incorporation degree of heavy metal in synthesized Portland cement was determined by total heavy metal analysis. The total heavy metals were analyzed via US EPA method 3052 and measured the concentration of heavy metals species by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The synthesized clinkers samples (0.5 g) were digested in 9 mL of concentrated nitric acid and 3 mL of hydrofluoric acid for 15 minutes using a laboratory microwave digester. A specific temperature profile was programmed such that the temperature of 180 ± 5 ºC must be reached in approximately less than 5.5 minutes and maintained for 9.5 minutes for the completion of the reaction. After cooling, the vessel contents were filtered through 0.45μm filter papers, diluted to volume, and measured by ICP-AES (US EPA, 1996).

Figure 3.10 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

3.3.2 Leaching of heavy metals form co-processed Portland cement

3.3.2.1 Preparation of mortar for leaching test

The cement samples are mixed with gypsum at cement to gypsums ratio= 95/5. Then, the mixing cement is blended with sand by using cement to sand ratio at 1/2.75. After that, water is added with a water-cement ratio of 0.485 for all samples. The samples are put into specimen molds following in ASTM C 109M-05. Specimen Molds, for the 2-in. or [50-mm] cube specimens shall be tight fitting. Finally, the mortars are cured at 20 °C for 3, 7, 14 and 28 days and brought the sample to test the compressive strength and the results are compared with Thai standard. After compressive strength testing, the cracking samples were grinded and applied for sequential extraction procedure, wet extraction test and toxicity characteristic leaching procedure.

The concrete specimens were used in Monolithic leaching test and were stored in closed molds for 28 days. The physical properties considered are the moisture content, the water absorption capacity (WAC–determined by mass balance of the specimens during the Monolithic leaching test) and the density (kg/m^3). The water open porosity of the material is assessed by determining its water absorption capacity (WAC).

3.3.2.2 Regulatory leaching of heavy metals from synthesized PC clinker and Mortar

The synthesized Portland cement clinker and cement mortar were analyzed for assessing the environmental risk by regulation leaching test. The regulation leaching tests consist of wet extraction test (WET) and toxicity characteristic leaching procedure (TCLP).

a) Wet extraction test (WET)

The wet extraction test is described in the Notification of the Ministry of Industry B.E 2548 (2006) by Thailand’s Department of Industrial Works (DIW) [7]. About 50 g of sample was weighted into polypropylene bottles. 500 ml of 0.2 M sodium citrate solution (adjusted to pH 5 ± 0.1 with 4.0 M NaOH) was added and agitated at room temperature for 48 hours. The extract was filtered through a 0.45 µm membrane filter, preserved by HNO_3 and stored at 4 ºC. The concentration of heavy metals was determined by ICP-AES (DIW, 2006).

b) Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test employed in this study followed the standard procedure described by the USEPA (1992). About 10 g of the sample was weighed and placed into each of the polypropylene bottles. About 200 ml of the TCLP No. 2 leachant (0.1 M HOAc at pH 2.88) was added. The bottles were tumbled at 29 ± 1 rpm in a rotary extractor at room temperature for 18 hours. At the end of the extraction, the leachate was filtered with GF/C glass fiber filter paper. The pH of the filtrate was measured and the leachate was acidified by a small amount of concentrated nitric acid to a pH of less than 2 before subsequent analysis by ICP-AES (US EPA, 1992).

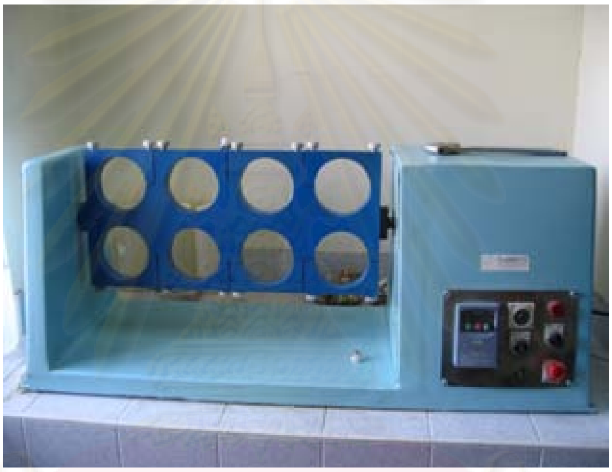


Figure 3.11 A rotary extractor for TCLP and WET

3.3.2.3 Heavy metals speciation in synthesized PC clinker, cement paste, and mortar by BCR sequential extraction procedure

The sequential extraction test was adapted from Tessier et al. The heavy metals are partitioned into the following five operationally defined fractions. All of samples were analyzed by ICP-AES.

Fraction 1 (F1-exchangeable): The sample was extracted with 0.5M $MgCl_2$ at pH 7.0 at a solid-to-liquid ratio of 1:8 with continuous agitation for 5 hours at room temperature. The extract was filtered through a 0.45 µm cellulose nitrate filter and stored at 4ºC. The solid residue was washed with deionized water, dried at 105ºC, and employed in fraction 2.

Fraction 2 (F2-bound to carbonates): The residue from F1 was extracted with 1 M NaOAc (adjusted to pH 5.0 with HOAc) at a solid-to-liquid ratio of 1:8 with continuous agitation for 5 hours at room temperature. The extract was filtered through a 0.45 µm cellulose nitrate filter and stored at 4ºC. The solid residue was washed with deionized water, dried at 105ºC, and employed in fraction 3.

Fraction 3 (F3-bound to iron and manganese oxide): The residue from F2 was extracted with 0.04M $NH_2.OH.HCl$ in 25% (v/v) HOAc (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 hours at 96°C and cooled. The extract was filtered through 0.45 µm cellulose nitrate filter and stored at 4ºC. The solid residue was washed with deionized water, dried at 105ºC, and employed in fraction 4.

Fraction 4 (F4-bound to organic matter/sulfide): The residue from F3 was extracted with 30% H_2O_2 (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 h at 85°C, and then extracted with 3.2 M NH_4OAc in 20% (v/v) HNO_3 with continuous agitation for 30 minutes. The extract was filtered through 0.45 µm cellulose nitrate filter and stored at 4ºC. The solid residue was washed with deionized water, dried at 105ºC, and employed in fraction 5.

Fraction 5 (F5-residual fraction): The residue from F4 was digested with USEPA SW-846 Method 3052.

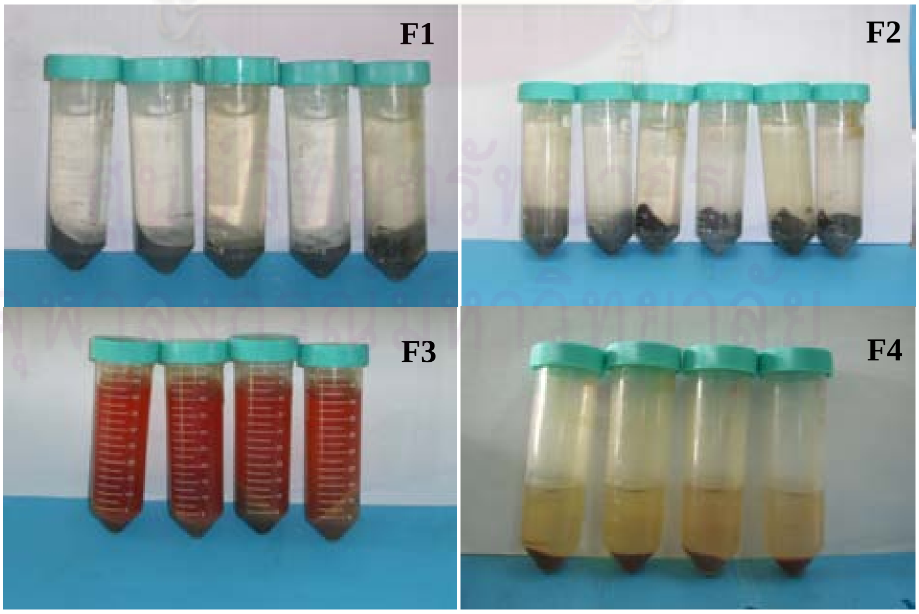


Figure 3.12 The sequential extraction sample

3.3.2.4 Leaching behavior of heavy metals from co-processed cement mortar by pore water (PW) test.

The Pore water test (PW) describes the initial equilibrium composition of the pore solution and the soluble species Maximum mobile fraction (MMF) for leaching. The test allows the assessment of the soluble constituent at steady state conditions between fine crushed material and demineralized water in closed vessels and for different liquid/solid ratios (L/S) at room temperature during 7 days of continuous stirring. The materials were crushed to less than 0.1 mm and samples were put into contact with demineralized water, for L/S ratios: 100, 50, 20, 10, 5, 1 and 0.5 ml/g (dried material). The closed vessels were agitated for 7 days by an end-over-end tumbler. After filtration (filter porosity, 0.45 mm) the solution is analyzed. The plotting of pH according to the L/S ratio, as well as the plotting of pollutant concentrations (mg/l) vs. L/S ratio gives useful information on the available quantities and solubility of different elements.

3.3.2.5 Leaching behavior of heavy metals from co-processed cement mortar by acid neutralization capacity (ANC) test

The applied Acid neutralization capacity test (ANC) is to examine the influence of pH on the leacheability of inorganic constituents from modified cement by addition of predetermined amounts of acid or base to reach desired end pH values in apparent steady state condition. The test is carried out on finely crushed materials in order to rapidly reach solid/liquid steady state conditions. Finely crushed material (grain size less than 1 mm) is in contact with a leachant volume at a determined pH; the same liquid/solid ratio is maintained for all the parallel running samples. In order to cover a wide pH range, it used nitric acid (non-complexing and only slightly oxidizing) and sodium hydroxide. A previous study enabled us to choose a 7 days liquid/solid contact time to reach a steady state at room temperature under agitation by an end-over-end tumbler. After filtration (filter porosity, 0.45 µm) the solution is analyzed. Plotting of the final pH according to the initial acid or base amount, as well as plotting of the pollutant concentrations (mg/l) according to the final elute pH, gives us useful information on the global response of the studied material with regard to an acidic aggression of the medium (alkaline capacity) as well as for each analyzed pollutant.

3.3.2.6 Leaching behavior of heavy metals from co-processed cement mortar by NEN: 7375 (Monolithic leaching test)

The Monolithic leaching test (ML) permits to evaluate the leaching behavior of monolithic wastes under dynamic conditions. It gives detail of dominant release mechanisms of inorganic constituents from regularly shaped specimens of monolithic wastes. This test is based on the Tank leach test NEN 7375. The test was conducted simultaneously on monolithic cubic specimens (5x5x5 cm^3) at 28 curing days. The leachant is demineralized water. The Liquid/Surface ratio of 10 m^3 /m^2 is maintained constant for each leachant renewal. The solutions are renewed after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. Therefore, these eluates analyzed after filtration (0.45 mm): pH, concentrations of the different species. All of results were analyzed by leaching model to explain the heavy metals behavior. This research interested in cadmium, chromium, and nickel.

Figure 3.13 NEN 7375 samples

3.3.2.7 Leaching model of heavy metals from co-processed cement mortar: case study of Cd, Cr, and Ni

The leaching model of heavy metals assumed the diffusion equations to explain the release of chemical in porous matrix. Diffusion is the process by which matter is transported from one part of system to another as a result of random molecular motions. The leaching model of Portland cement mortar referred to the chemical nature of the source and the environmental factors including conditions of contact materials, leachant, and the eluate physical and chemical characteristics. In order to formalize the materials scenario system, it is requirement to identify the main chemical species, reactions and transport mechanism.

In the case of cement materials, the main mineralogical species responsible for the calcium release is the Portlandite ($Ca(OH)_2$). After the Portlandite depletion, the hydrated-calcium–silicates (CSH) control the calcium solubility. The solid heavy metal speciation is not known, it may be incorporated in CSH or as heavy metal oxide. The ANC results show the difficulty to assign the observed solubility to a presumed solid phase.

The dissolution/precipitation processes begin at the solid/pore water interface together with chemical reactions in the aqueous phase when immersed in water. At the same time, the soluble chemical species migrate in the pore solution due to concentration gradients from the core to the surface of the material and are found in the eluate. The eluate is chemical complex, the same reactions as in the pore water may occur. The contact time with the material and the hydrodynamics of the liquid phase are important parameters for the system evolution (element depletion in the material, eluate pH, eluate saturation in weak soluble elements).

The proposed leaching model is developed on the basis of a solid/liquid reactor with solution renewal (Figure 3.14) (Tiruta-Barna, Imyim, and Barna, 2004). It presents two modeling levels: (i) a coupled chemical reaction-transport model for the water saturated porous matrix and (ii) a coupled chemical reaction transport model for the eluate in a continues stirred reactor, open or batch.

For this study, six major species are considered according to material’s composition: Ca, Na, K, Cd, Cr and Ni. The laboratory results of M2 were employed as case study. The coupled dissolution/diffusion model takes into account:

1. The release of soluble species (Na^+, K^+) by diffusion;
2. The release of calcium using a local dissolution/ precipitation equilibrium of Portlandite and/or CSH and transport by diffusion in the pore solution;
3. the release of heavy metal species (Cd, Cr, and Ni) using a local dissolution/precipitation, complexation reaction and diffusion in pore solution;
4. the hypothesis of local equilibrium, i.e. the reactions taking place in a homogenous liquid are reversible and much quicker than transport phenomena. Therefore, the solution (pore water, eluate) is considered to be in equilibrium at each point in space and time
5. the simultaneous calculation of pH of the pore solution (local) and reservoir water by the electroneutrality equation; and
6. Debye–Hückel activity model is used to calculate the thermodynamic equilibrium in the pore solution and in the eluate.

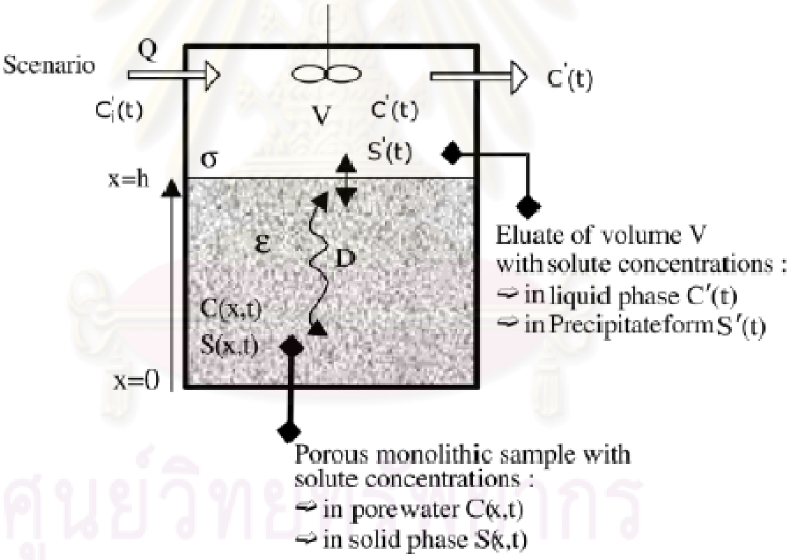


Figure 3.14 Simplified scheme of the leaching process(Tiruta-Barna, Imyim, and Barna, 2004)

The porous matrix contains time and space-variable concentrations of the dissolved species *C*(*x*,*t*) and in the solid phases *S*(*x*,*t*). The same chemical species exist in the eluate with the concentration C' (*t*) and S' (*t*). The eluate may be steady or renewed (flow rate *Q* or sequential renewal) and its composition at the reservoir inlet is $C_i'(t)$. In the *porous matrix*, the soluble species diffuse under the effect of a concentration gradient on the *x* axis (Figuer3.14) and participate in chemical equilibrium in solution (pore water) and in precipitation/ dissolution reactions. Fick’s second law (equation 3.4) was employed to predict how diffusion causes the concentration field to change with time.

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \qquad 3.4$$

Where D represents the observed diffusion coefficient of the considered element.

The boundary conditions are:
– In the center of the material (*x* = 0):

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0 \qquad 3.5$$

– At the eluate/material apparent interface (*x* = *h*)

$$D\left.\frac{\partial C}{\partial x}\right|_{x=h} = k_t\,(C' - C|_{x=h}) \qquad 3.6$$

where k_t (m/s) is the mass transfer coefficient between the eluate and the pore water at the surface of the material. The kinetic equations (Equation3.7) are added to the above equations that describe local precipitation/ dissolution phenomena:

$$\begin{cases} \dfrac{\partial S}{\partial x} = k\,(C - C_{eq}) \text{ if } S > 0 \text{ or } (S=0 \text{ and } C > C_{eq}) \\ \dfrac{\partial S}{\partial t} = 0 \text{ if not} \end{cases} \qquad 3.7$$

In the *eluate*, the accumulation of an element is determined by the flux from the material, by transport through convection (with eluate flow rate *Q*) and by precipitation/dissolution reactions of solid phases containing the element.

$$\frac{\partial C'}{\partial t} = \frac{k_t \rho A}{V}\,(C|_h - C') - \frac{\partial S'}{\partial t} - \frac{Q}{V}\,(C' - C_i') \qquad 3.8$$

$$\begin{cases} \dfrac{\partial S'}{\partial x} = k\,(C' - C'_{eq}) \text{ if } S' > 0 \text{ or } (S'=0 \text{ and } C' > C'_{eq}) \\ \dfrac{\partial S'}{\partial t} = 0 \text{ if not} \end{cases} \qquad 3.9$$

C_{eq} and C'_{eq} are the saturation concentrations of pore solution and leachate. Two electroneutrality equations are added for the two liquid phases, the pore water and the eluate in the general form:

$$\sum z_+ C_+ + C_{H+} = \sum z_- C_- + C_{OH-}$$
$$\sum z_+ C'_+ + C'_{H+} = \sum z_- C'_- + C'_{OH-} \qquad 3.10$$

According to the local equilibrium hypothesis, the kinetic constant k (mol/m^{3}s) has a high value such that the dissolution/ precipitation kinetics do not limit the evolution of concentrations in the pore water (rapid reactions) and such that mass flux is only determined by diffusion. Equations (*equation 3*.7 and *equation 3*.9) ‘pilot’ the sense of reactions:

- If $C > C_{eq}$, the solution is supersaturated and precipitation occurs,
- If C-Ceq, the solid dissolves (if present).

The external mass transfer process is more rapid than the diffusion process, and then the transfer coefficient k_t may be set at a sufficiently high value not to affect the diffusion flux towards the eluate. The equilibrium concentrations C_{eq} and C'_{eq} are calculated from equilibrium constants (solubility product). The pH-dependent equation determined from ANC test was used in the case of heavy metals.

The partial-differential-equation system was solved in MATLAB using the method of finite-differences: a forward scheme for the space variable and the Gear method for the time variable were employed.

The unknown parameters of the model are the observed diffusion coefficients D for each element. The model was applied for the simulation of the dynamic leach test (ML) in order to determine the effective diffusion coefficients. In the ML test the element concentrations C'_{exp}, were experimentally monitored vs. time. The diffusion coefficients of each species are evaluated by the best consistency of a simulated eluate concentrations $C'(t)$ and the experimental ones $C'_{exp}(t)$.

The input values for the behavioral model parameters are supplied by the proposed leaching tests:

- The initial concentration of each soluble species in the pore solution from PW test.
- The initial quantity of each solid phase from ANC and MMF test.
- The pH-dependent solubility of weakly soluble species from ANC test for heavy metals.

- The physical parameters: eluate volume *(V)*, monolith surface (*A*), porosity (ρ), and the released concentrations (C'_{exp}) from the ML test.

The calculated average flux of relevant species (mmol/m^2 s) are plotted vs. *Ti* which is defined for each leaching sequence by

$$Ti = \left(\frac{\sqrt{t_i} + \sqrt{t_{i+1}}}{2} \right)^2 \qquad 3.11$$

The simulated pH is a global control parameter for the model, because it is calculated from the electroneutrality condition involving simulated concentrations of all species in solution. The simulated pH and fluxes reproduce very well the experimental values and illustrate the performance of the proposed coupled chemical transport model.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Raw material analysis

4.1.1 Raw meal

The raw meal was collected from Siam City Cement Public Company Limited in Saraburi. The chemical compositions of raw meal were given in Table 4.1. Quality of Portland cement clinker depends on its raw meal chemical composition. Contents of oxides in the raw meal are approximately 15% SiO_2, 3% Al_2O_3, 3% of Fe_2O_3 and 42 % CaO. Lea (2004) provided typical ranges of chemical compositions for raw meal as follows: 6.9-15.9 % SiO_2, 1.9-4.7% Al_2O_3, 0.6-1.9% of Fe_2O_3 and 41.7-49.0 % CaO. The chemical compositions of the collected raw meal were illustarated in Table 4.1 together with those from the literarture as a comparison. It is apparent that the chemical compositions of the raw meal were appropriate for synthesizing clinker in this research.

Table 4.1 Composition of the raw meal via X-ray fluorescence spectrometry

Chemical Composition	%	Ideal composition of raw meal,%	Minimum composition of raw meal,%	Maximum composition of raw meal,%
SiO_2	15.0	14.0	6.9	15.9
Al_2O_3	3.2	4.1	1.9	4.7
Fe_2O_3	2.5	1.6	0.6	1.9
CaO	42.2	43.2	41.7	49.0
MgO	1.3	NA	NA	NA
K_2O	0.3	NA	NA	NA
Na_2O	0.1	NA	NA	NA
SO_3	0.2	NA	NA	NA
P_2O_5	0.1	NA	NA	NA
Cl	0.01	NA	NA	NA
TiO_2	0.2	NA	NA	NA
Mn_2O_3	0.1	NA	NA	NA
LOI	34.5	NA	NA	NA

NA: Not-Available

4.1.2 Grinding sludge

A local waste collector supplied the grinding sludge for use in this research. This sludge, which was a residue from grinding process, was generated by iron forging industry. Chemical composition of the grinding sludge was determined and is shown in Table 4.2. Desired alternative raw materials for cement production must contain compounds that consist mainly of silica, alumina, and iron; undesired compounds are sulfur, chloride, and heavy metals. The Thai cement company controls the pH, sulfur content, and chloride content. The pH should be less than 4, while the sulfur and chloride content must be less than 2.5% (w/w) and 0.5 %(w/w), respectively. According to Thailand regulations set by the Department of Industrial Works, under the Ministry of Industry, this sludge is a hazardous waste and has the waste code number 12 08 18 HA (metal sludge [grinding, honing, and lapping sludge] containing oil) (DIW, 2006). As shown in Table 4.3, the concentrations of heavy metals such as cadmium, chromium, mercury, and nickel in this sludge were higher than the Thai regulation values. It was found that there were high concentrations of iron and manganese. For the local cement company, an interesting alternative raw material must contain more than 50 % iron (w/w). It is suggested by other researchers that the reactivity of cement increases at high heavy metal contents (Kolovos, Tsivilis and Kakali, 2002). Thus, the high heavy metal content in the sludge can mean it has the potential to be applied as an alternative raw material in the cement industry. This research focused on the high concentrations of heavy metals namely cadmium (Cd), chromium (Cr), nickel (Ni), and manganese (Mn) in synthesized clinker. Mercury (Hg) was excluded because volatile heavy metals such as mercury do not become incorporated into clinker.

Table 4.2 Chemical composition of the grinding sludge

Chemical composition	**% (w/w)**
Al_2O_3	4.74
CaO	0.34
Fe_2O_3	74.68
MgO	0.04
SiO_2	15.28
K_2O	0.28
Na_2O	0.55
SO_3,%	0.55
Chloride content (mg/kg)	ND
pH	8.85
Heating Value (Kcal/kg dry weight)	≈7,000-8,000

ND: Not detected

Table 4.3 Trace heavy metals in the grinding sludge compared with Thai regulations set by the Department of Industrial Works, Ministry of Industry

Trace Element	Concentration (mg/kg)	Thai Regulations
Chromium (Cr)	8,190	< 2,500
Cadmium (Cd)	707	< 100
Copper (Cu)	950	< 2,500
Lead (Pb)	74.00	<1,000
Manganese (Mn)	62,827	ND
Mercury (Hg)	27	< 20
Zinc (Zn)	475	< 5,000
Thallium (Tl)	26	< 700
Vanadium (V)	96	< 2,400
Nickel (Ni)	2,291	< 2,000

ND: Non detected

4.2 Effects of grinding sludge on synthesized Portland cement clinker

4.2.1 Effect of grinding sludge on burnability

The content of free lime in the clinker is a significant indicator of the clinker burning process. The utilization of alternative raw materials containing heavy metals can affect not only burning process but also properties of clinker. The free lime is a parameter to basically evaluate the properties of clinker and burning ability or burnability (BC). Decrease in free lime means an improvement in the burnability, while a rise in the free lime means the deterioration in the burnability. The content of free lime can also change when CaO takes place in a reaction that leads to a new compound.

Free calcium oxide in small amounts (usually below 1 wt.%) is a regular constituent of Portland clinker, but larger amounts may be present if the maximum temperature in the production of the clinker is too low, the burning time is too short, or the CaO content in the raw material exceeds the acceptable range (lime saturation factor >100). Large amounts may cause expansion, strength loss and cracking of the hardened paste, due to a delayed hydration of free calcium oxide to calcium hydroxide, which takes place and is associated with an increase in volume. Thus, excessive amounts of free calcium oxide in clinker must be avoided (Raupp-Pereira, et al., 2008).

The analyzed contents of free lime in the clinker at different temperature were shown in Table 4.4 and Figure 4.1. The ratio of the burnability capacity of sintered samples to the burnability capacity of the pure sample (M0), in relation to the substitution of grinding sludge in the raw meal is presented in Figure4.1. Figure 4.2 presents the ratio [fCaO Mi (T2) – fCaO Mi (Tl)]/ [fCaO M0 (T2)-fCaO M0 (Tl)] at different temperature ranges in relation to the sludge content(Mi is M1, M2, and M3). Figure 4.3 showed the BC ratios of greater than 1 indicating that the added mineral favored the sintering process.

The replacement of grinding sludge in the raw meal decreased the clinkerization temperature. As can be seen from Table 4.4, the amount of free lime between 1400°C and 1450°C were found to be approximately 0.6-1.3 %, the free lime levels below 1% in an ideal clinker (Trezza and Scian, 2000; Lin ans Lin, 2005; Raupp-Pereira, et al., 2008) and 1.5% in a real clinker (Potgieter, Horn, potgieter, and

Wirth, 2002) are considered acceptance. The replacement of the grinding sludge blends in the conventional cement raw meal improves the burnability. Surprisingly, a positive impact was recorded even from 1200 °C, attributed to the presence of Cd, Cr, Mn, and Ni in the sample. An important decrease in the free lime content was recorded at 1400°C and 1450°C (by 35-45%, and 18-32%, respectively). A remarkable impact of the replacement of grinding sludge on the reactions supported the presence of the liquid phase. This was also reflected on the BC values (Figure 4.3), which were mainly based on the free lime content at 1450°C and 1400°C. On the overall, the substitution of grinding sludge was considered to improve the burnability of raw meal in low temperature. As shown in Figure 4.1, the substitution of grinding sludge in the raw meal lowered the clinkerization temperature. The substitution of grinding sludge of more than 3% in the raw mix did not affect the burnability. From the graphs in Figure 4.2, we can see that this ratio demonstrated the effect of grinding sludge content on the rate of the free lime consumption and it is assumed to be 1 at all temperature ranges for the pure sample. As it was observed, grinding sludge decreased the rate of the free lime reaction in the range from 1200°C to 1450°C except the range between 1100 and 1200°C. Moreover, it can be seen that the free lime contents of synthesized Portland cement clinker with grinding sludge were lower than that without the grinding sludge. These results explained that the utilization of grinding sludge can enhance the adsorption of free lime, improve the burnability of Portland cement and accelerate the formation in the clinker production.

If burnability was used as the ma in criteria for selecting the optimal temperature for synthesized clinker, it can be concluded that both 1400°C and 1450°C were suitable temperatures. However, the proper temperature was chosen at 1400°C due to the fact that the high-temperature furnace could be damaged at higher temperature.

Table 4.4 f *CaO* and Brunability capacity (BC) values of the synthesized clinker

Sample	*f* CaO							
	Temperature (°C)							
	1450	1400	1350	1300	1200	1100	C	BC
M0	0.89	1.27	2.02	3.43	13.66	31.12	114.77	5.23
M1	0.73	0.83	1.36	2.06	11.90	31.96	104.12	5.76
M2	0.68	0.71	0.88	1.35	9.22	31.57	93.36	6.43
M3	0.61	0.69	0.71	1.07	8.76	31.66	90.86	6.60

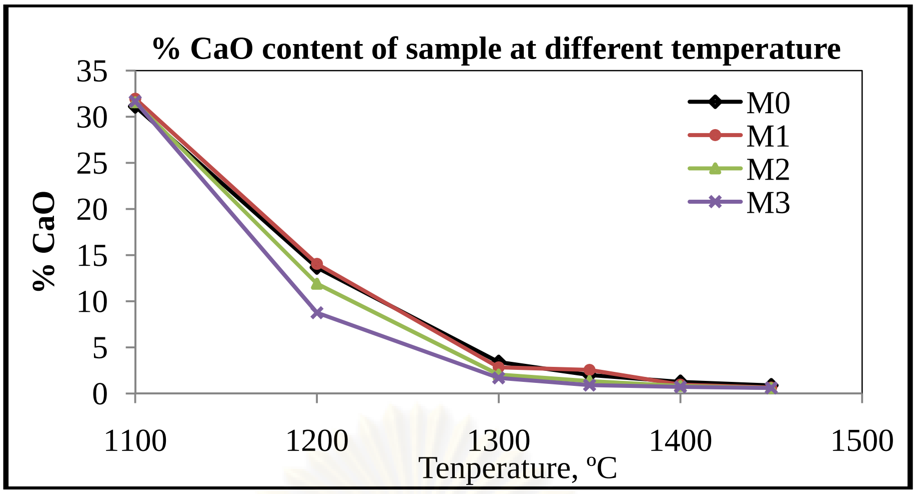


Figure 4.1 Free lime content ant different times

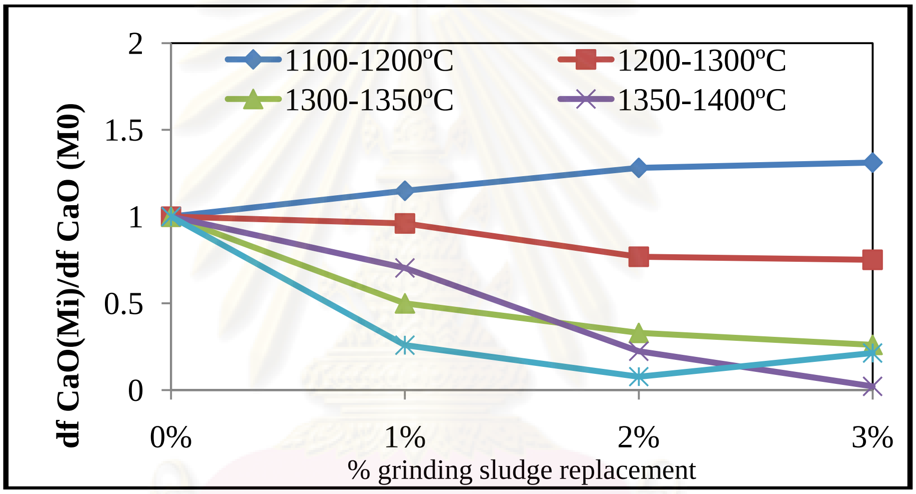


Figure 4.2 The ratio [*fCaO*Mi (T2)-*fCaO*Mi (Tl)]/[*fCaO* M0 (T2)- *fCaO* M0 (Tl)] at different temperature ranges in relation to the sludge content (i: percent sludge replacement)

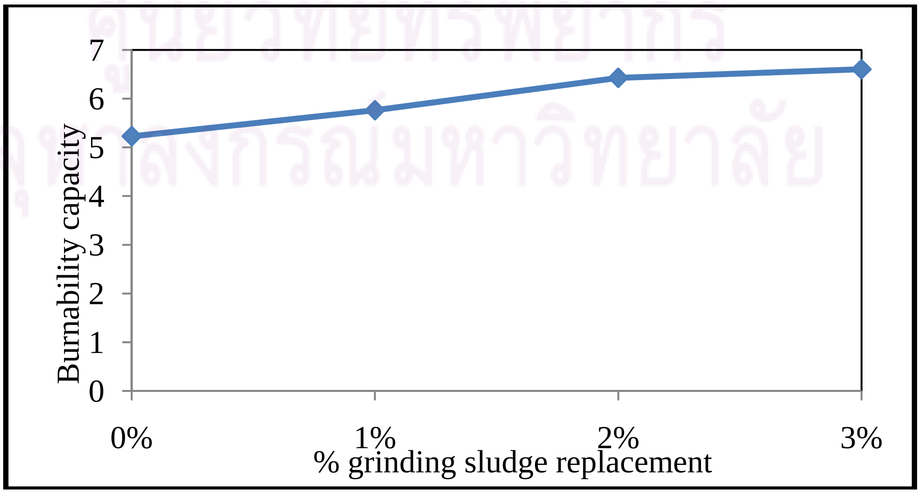


Figure 4.3 Brunability capacity in relation to the percent of grinding sludge replacement

4.2.2 Effect of grinding sludge on chemical composition at different burning temperatures

The synthesized PC clinker from 4.2.1 were measured the chemical compositions in oxide form by X-ray fluorescence spectroscopy (XRF). The modulus parameters and bogue equations are indirect techniques to converts chemical analysis to potential phase composition. The modulus parameters and bogue equations must calculate from the percent of chemical oxide and are explained as equation 4.1 to 4.7. The controlled value was explained in Table 4.5. The conventional cement product has controlled the amount of SiO_2, Al2O3, Fe2O3 and CaO at 18-22%, 4-6%, 2-4%, and 60-70% sequentially. The modulus parameters have limited value of LSF, SR, and AR at 90-101, 1.4-4.2, and 0.6-4.2 respectively. The Bogue parameters have restricted the amount of C_3S, C_2S, C_3A and C_4AF at 55-66%, 15-25%, 8-14% and 8-12%.

Modulus parameters

Lime saturation factor (LSF) $= CaO/ (2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3)$ 4.1

Silica Ratio (SR) $= SiO_2/ (Al_2O_3+Fe_2O_3)$ 4.2

Alumina Ratio (AR) $= Al_2O_3/Fe_2O_3$ 4.3

Bogue Equations

$C_3S = 4.07CaO-7.60SiO_2-6.27Al_2O_3-1.43Fe_2O_3-2.85SO_3$ 4.4

$C_2S = 2.87SiO_2-0.75C_3S$ 4.5

$C_3A = 2.65Al_2O_3-1.69Fe_2O_3$ 4.6

$C_4AF = 3.04\ Fe_2O_3$ 4.7

Table 4.5 The value controlled parameter of cement product parameter

Chemical Compound	Product Range values		Modulus and Bogue parameter	Product Range values	
	Min.	Max.		Min.	Max.
SiO_2	18%	22%	LSF	90	101
Al_2O_3	4%	6%	SR	1.4	4.2
Fe_2O_3	2%	4%	AR	0.6	4.2
CaO	60%	70%	C_3S	55%	65%
Sum	≈100%		C_2S	15%	25%
MgO, K_2O, Na_2O, SO_3, P_2O_5, Cl, TiO_2, Mn_2O_3	The entire content of minor components is commonly under 5%		C_3A	8%	14%
			C_4AF	8%	12%

The XRF results of synthesized PC clinker at different burning temperature were plotted between the percent sludge replacements and modulus and bogue parameters. They were shown in Figure 4.4 to Figure 4.8.

Figure 4.4 showed the graphs plotted between the amount of main oxide in the synthesized PC clinker at different temperature and percent of sludge replacement. While the amount of Fe_2O_3 had raised, the amount of CaO, SiO_2 and Al_2O_3 declined when the percent of sludge replacement increased.

It can be seen from the data in Figure 4.5 that the LSF values at 1100°C were significantly more than other results and maximum value for cement product. These results indicated that the decomposition CaO was low and the formation of cement phase was not complete. A decrement of 10% of LSF from 1100°C to 1200°C is an important concern. This concern associated with the free lime content in Table 4.4 which showed the free lime content reduced at 1200°C. It indicated that the formation of cement phases started. It was obvious that the LSF results at 1400°C and 1450°C stayed between the minimum and maximum cement product values. However, the decreases in SR and AR in Figure 4.6 and Figure 4.7 were normal phenomena when there is addition of Fe_2O_3. This is because SR and AR ratios are the proportion that divided by the amount of iron oxide. The higher the grinding sludge utilized, the lower SR and AR must occur.

Figure 4.8 provided the effect of grinding sludge on bogue parameters. The amount of C_3S, C_2S, C_3A, and C_4AF were roughly estimated by the proportion of main chemical oxide. The C_3S and C_2S have remained stable between 1100 °C and 1200°C when the sludge replacement increased .The C_3S at 1100°C were less than 1200°C while the C_2S was different. The C_2S at 1200°C were more than 1100°C. It related to the reaction of cement phases (in Figure 4.9) that the C_3S at 1100 °C was the unreacted free lime content and the C_2S usually formed at 1200°C. The C_2S reacted with CaO and formed C_3S at higher 1200°C. The effect of grinding sludge cause moderately decreased in C_2S and slightly supported C_3S when the burning temperature was higher than 1200°C. It is obvious that the amount of C_3S and C_2S at 2% of sludge replacement and 1400°C stayed in between the minimum and maximum cement product values. Moreover, C_3A had gone down but the C_4AF had gone up when the utilization of sludge increased. This waste promoted the formation of C_4AF and inhibited the formation of C_3A. It can be concluded that the burning temperature of 1400°C was the optimal temperature for synthesis of these PC clinker samples. The optimal temperature of 1400°C was used for all experiments that followed.

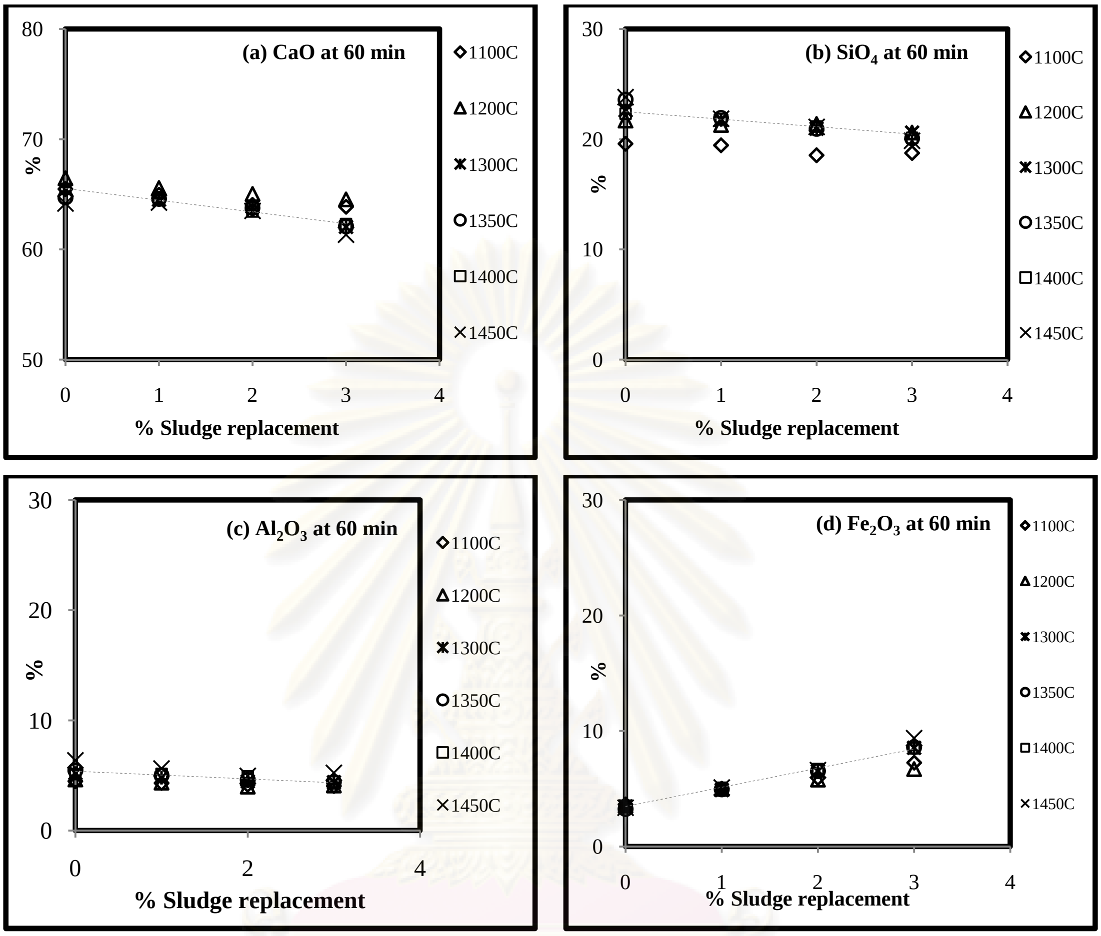


Figure 4.4 Amount of chemical oxides in synthesized PC clinker at different temperature (a) CaO (b) SiO_2 (c) Al_2O_3 (d) Fe_2O_3

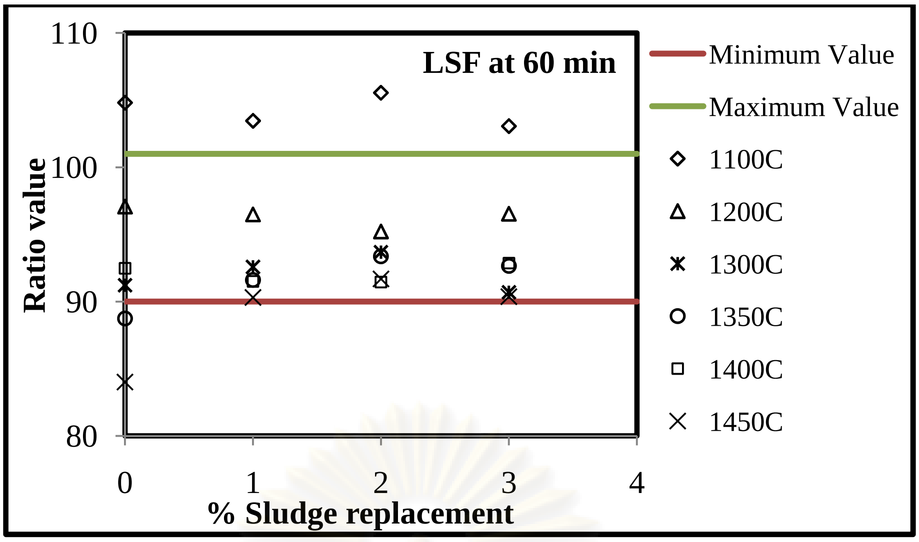


Figure 4.5 Ratios of LSF in synthesized PC clinker at different temperatures

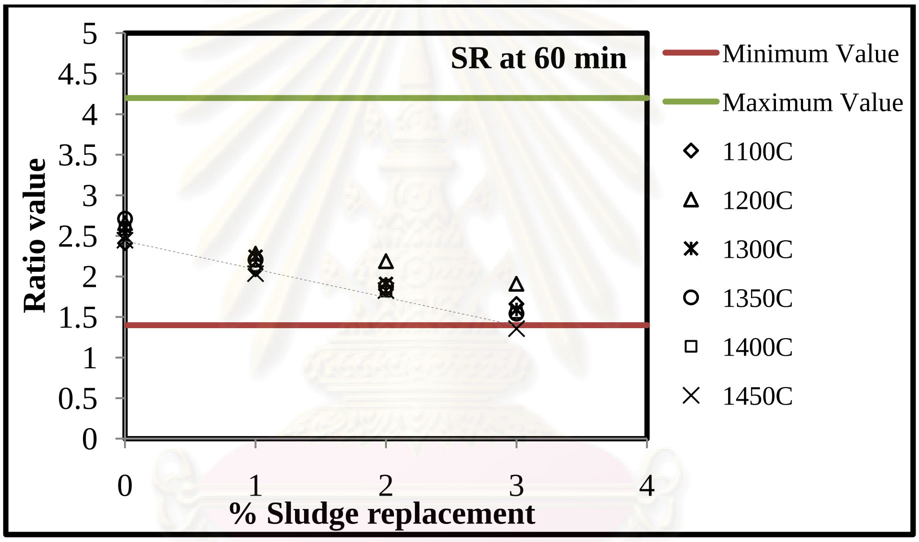


Figure 4.6 Ratios of SR in synthesized PC clinker at different temperatures

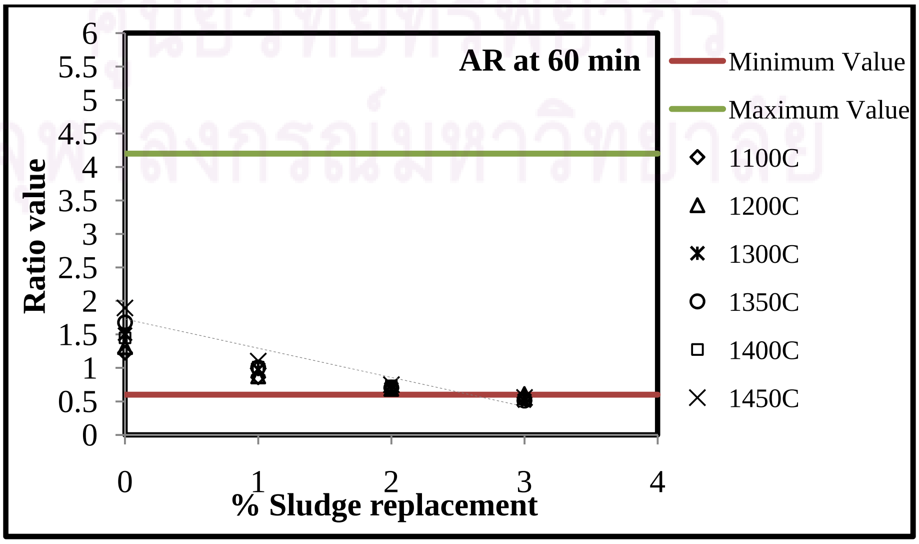


Figure 4.7 Ratios of AR in synthesized PC clinker at different temperatures

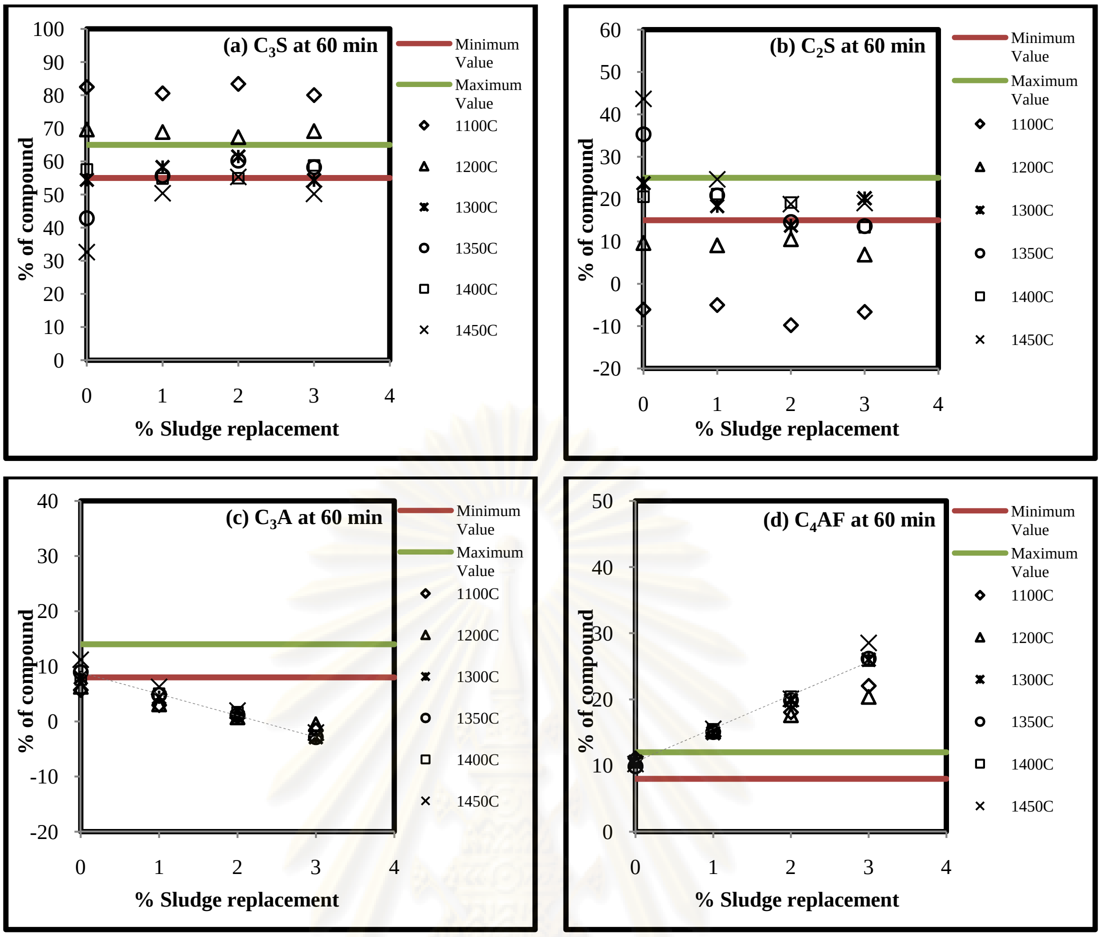


Figure 4.8 Amount of cement phases in synthesized PC clinker at different temperature (a) C_3S at 60 min (b) C_2S at 60 min (c) C3A at 60 min (d) C_4AF at 60 min

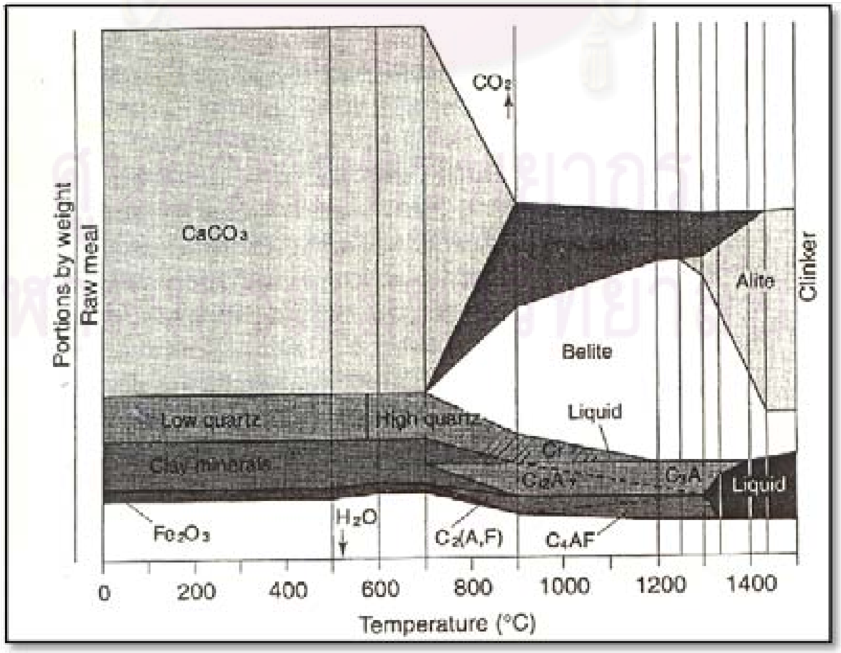


Figure 4.9 Reaction of raw meal at different burning temperature.

4.2.3 Effect of grinding sludge on chemical composition at different burning time

The results of chemical composition of synthesized PC clinker at 1400°C were shown in Figure 4.11. The LSF increased when utilization of sludge increased. It was found that all results at burning time 60 minutes remained in the cement production range. Nevertheless, the LSF at 30 minutes and 75 minutes gradually increased. It indicated that the optimal time was 60 minutes. Figure 4.12 and Figure 4.13 showed the SR and AR with the percentage of sludge. The most interesting finding was that the SR and AR decreased and stayed below the minimum value at 3% of sludge replacement. Figure 4.10 showed that the utilization of grinding sludge promoted the C_3S and C_4AF while inhibited C_2S and C_3A. All results were concluded that the optimal time is 60 minutes and the utilization sludge is limit at 2 % of sludge replacement.These results associated with Tsakiridis and colleague (2008). They studied on the utilization of steel slag for Portland cement clinker production and found that the reducing of C_2S and the increasing of C_4AF in clinker were occurred when there are the presence of impurity ions (Fe and Al).

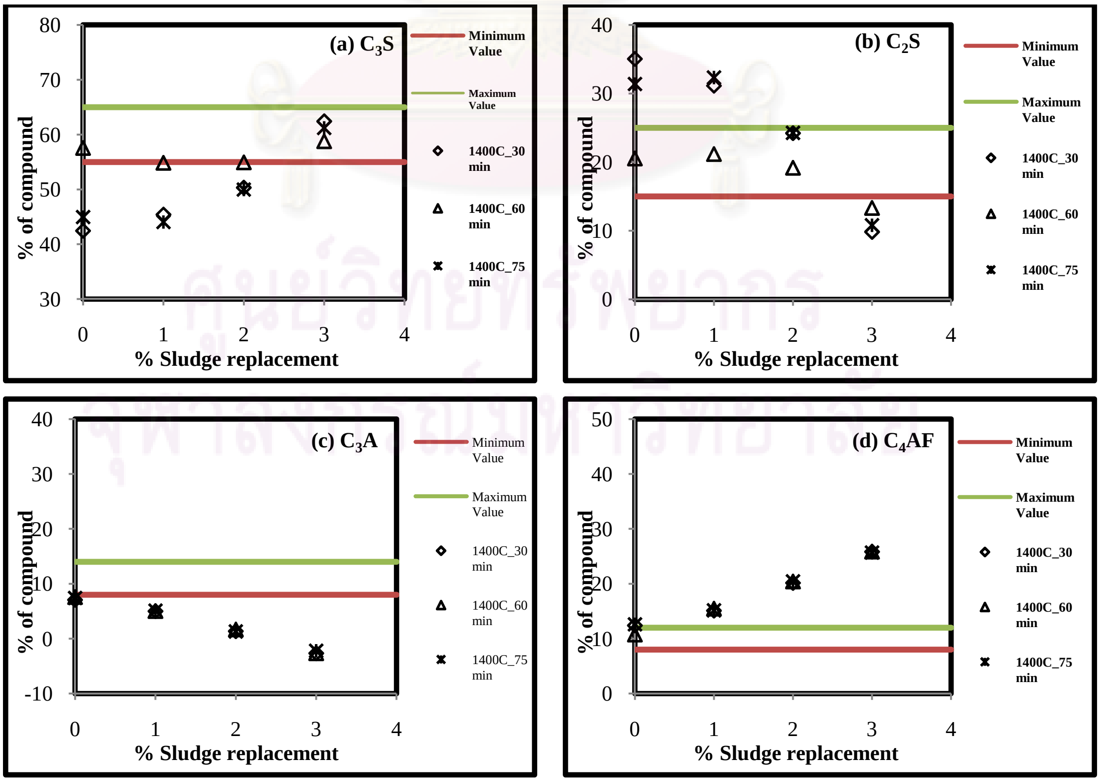


Figure 4.10 Amount of cement phases in synthesized PC clinker at different times

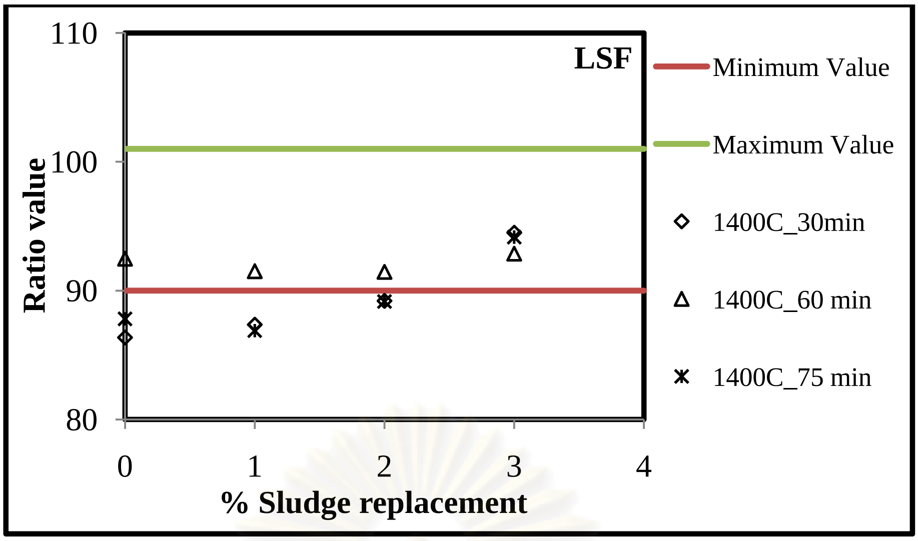


Figure 4.11 Ratios of LSF in synthesized PC clinker at different times

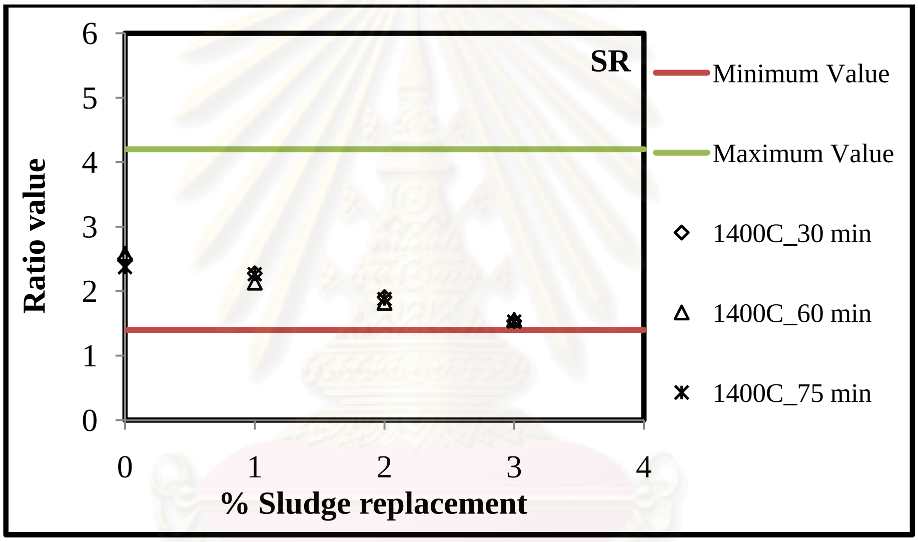


Figure 4.12 Ratios of SR in synthesized PC clinker at different times

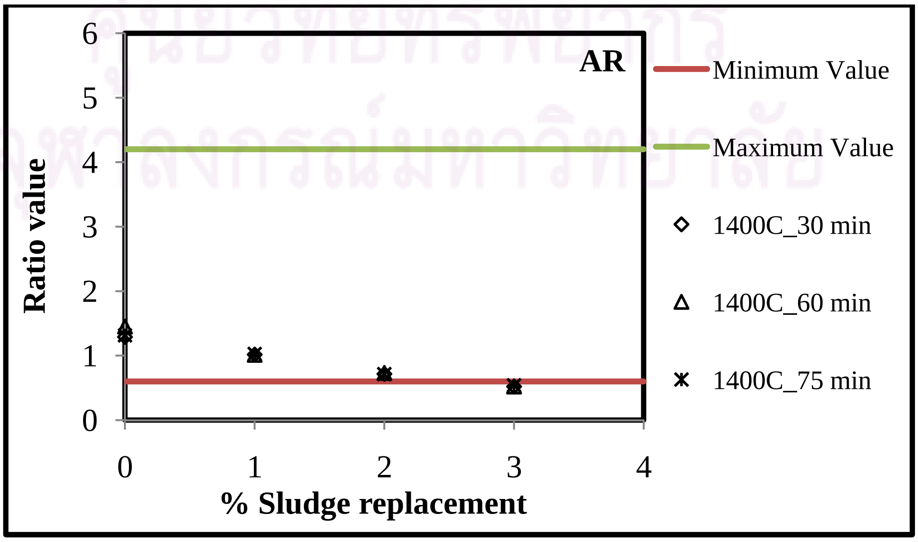


Figure 4.13 Ratios of AR in synthesized PC clinker at different times

4.2.4 Effect of grinding sludge on mineralogical composition at different burning temperature

The samples from section 4.2.1 were analyzed by X-ray diffraction spectroscopy (XRD) to explain the mineralogical composition of cement. The main chemical compounds of Portland cement product contained of C_3S, C_2S, C_3A, and C_4AF. These compounds generally formed in crystalline compound and gave peaks at common 2θ values. The reactions of Portland cement product with different temperature were explained in Figure 4.9. On the left-hand side, it showed that the feedstock comprise in the case, calcite ($CaCO_3$), quartz (SiO_2), clay mineral (SiO_2-Al_2O_3-H_2O) and iron oxide (Fe_2O_3). Up to a temperature of about 700°C, activation of the silicates through the removal of water and changes in the crystal structure takes place. Within the temperature range 700-900°C, decarbonation of the calcium carbonate occur, together with the initial combination of the alumina, ferric oxide and activated silica with lime. From 900 to 1200°C, belite forms. Above 1250°C and more particularly above 1300°C, the liquid phase appears and this promotes the reaction between belite and free lime to form alite. During the cooling stage (right- hand side of the diagram) the molten phase goes to a glass or, if cooling is slow, the C_3A crystallizes out and in extreme cases the alite dissolves back into the liquid phase and reappears as secondary belite. The favorite measuring of cement phase techniques consist of XRD and optical microscope (OM).

The XRD pattern of a commercial Portland cement was shown in Figure 4.14. Figure 4.15 were shown the XRD pattern of synthesized Sample M0 at different temperature at 60 minutes and Figure 4.16 were given the XRD pattern of synthesized Sample M0 at different temperature at 60 minutes. These data must be interpreted with caution because the phases of cement were complex compound. The results were analyzed by comparing with the XRD pattern of commercial Portland cement and the crystalline chemical in Figure 4.9.

The XRD patterns of M0 and M3 were different. The M0 at 1100°C consisted of lime, quartz, and Portlandite while the M3 contained of lime, quartz, calcium aluminum silicate ($Ca_2Al_2SiO_7$) and calcium magnesium aluminum silicate ($Ca_{54}MgAl_2Si_{16}O_{90}$). The compositions were similar to raw materials. The formation of cement phase did not occur. The C_2S and C_4AF formed from 1200°C to 1450°C on both M0 and M3. In addition, the C_3S formed at 1300°C. The utilization of grinding sludge did not influence crystalline formation of cement product. The optimal temperature was thus 1400°C.

Nonetheless, the intensity of commercial PC clinker was higher than the intensity of synthesized PC clinker. The high amount of C_4AF indicated that the iron oxide was able to combine with calcium and alumina to produce the ferrite phase upon cooling from liquid phase (Tsakiridis, el at., 2008; Shih, el at., 2005). Stephan et al. (1999 a) pointed out that heavy metal such as Ni, Cr, and Zn have no influence on the formation of clinker phases, even at concentrations that are 10 to 20 times higher than the concentrations observed in normal clinkers.

4.2.5 Effect of grinding sludge on mineralogical composition at different burning time

Figure 4.17 and Figure 4.18 explained the XRD pattern of M0 and M3 at different times, respectively. The intensity of M0 was higher than the intensity of M3. The effect of grinding sludge is apparent from Figure 4.18 that the C_2S in M3 was lower than M0. The brownmillerite peak in M3 is higher than M0. Nevertheless, the XRD pattern of M0 and M3 is similar to commercial PC clinker. The XRD peak at 60 minutes was higher than 30 and 75 minutes. It can be concluded that the optimal time was 60 minutes.

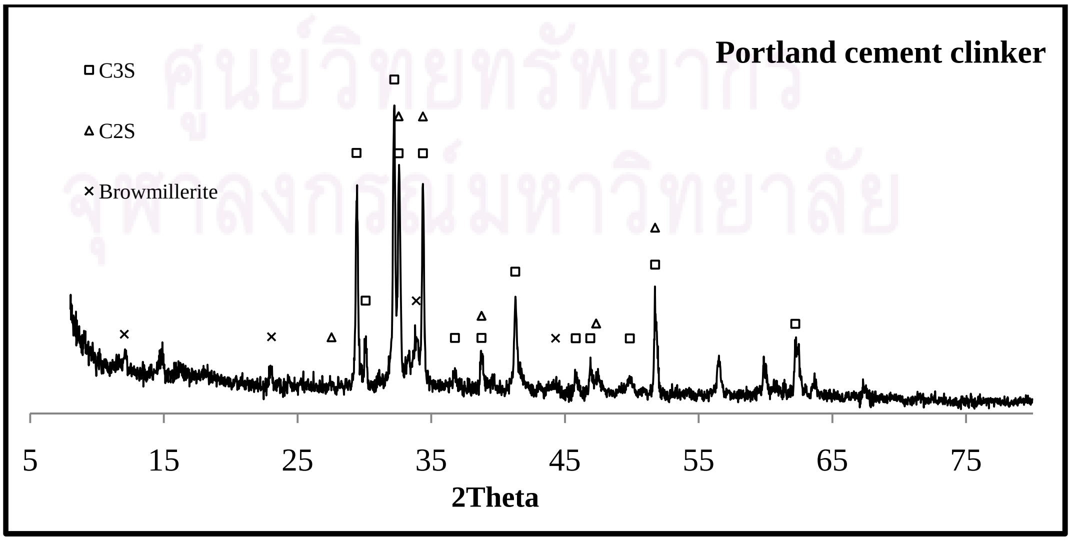


Figure 4.14 X-ray diffraction of clinker from local cement company

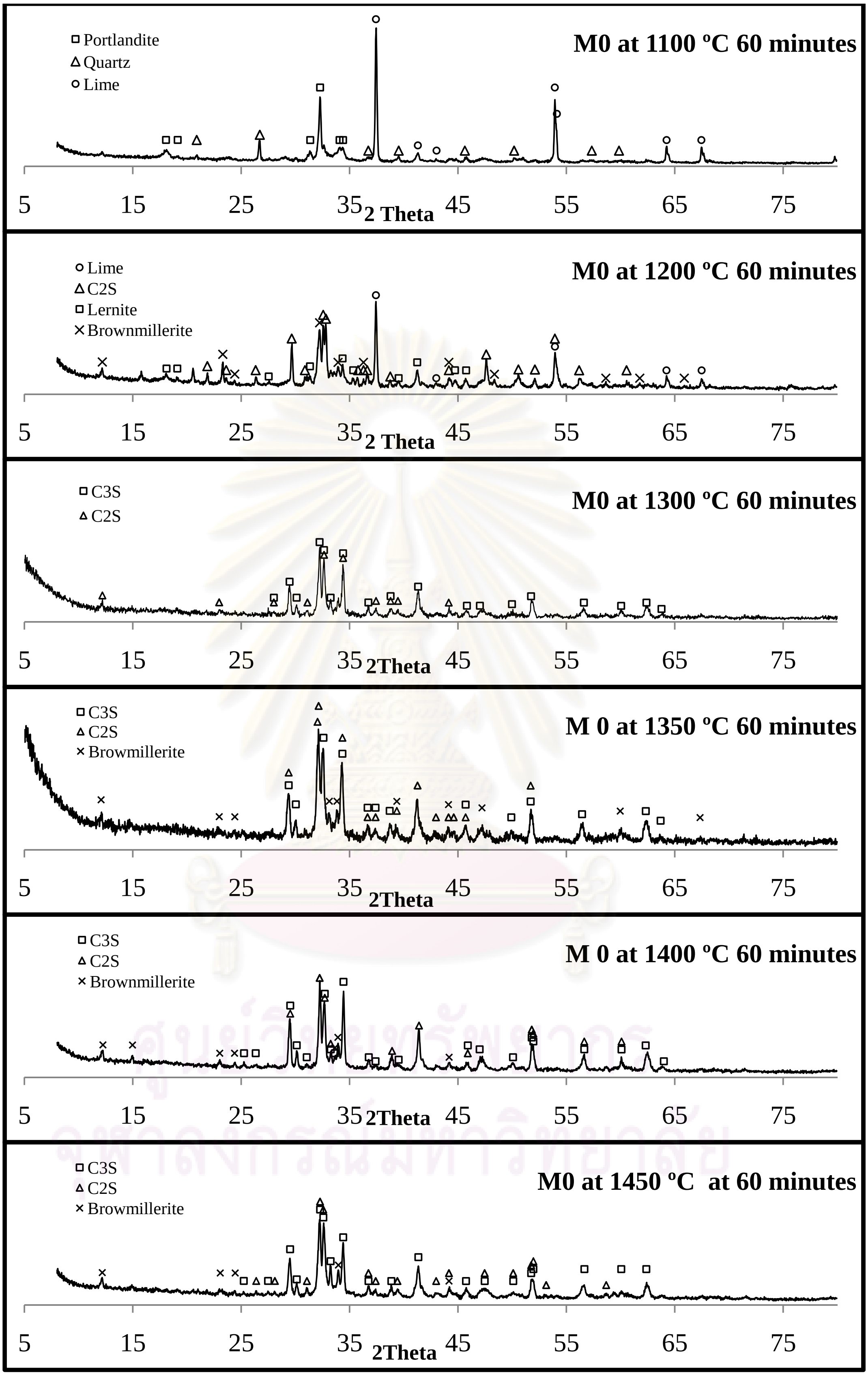


Figure 4.15 X-ray diffraction of clinker sample without grinding sludge at different burning temperature

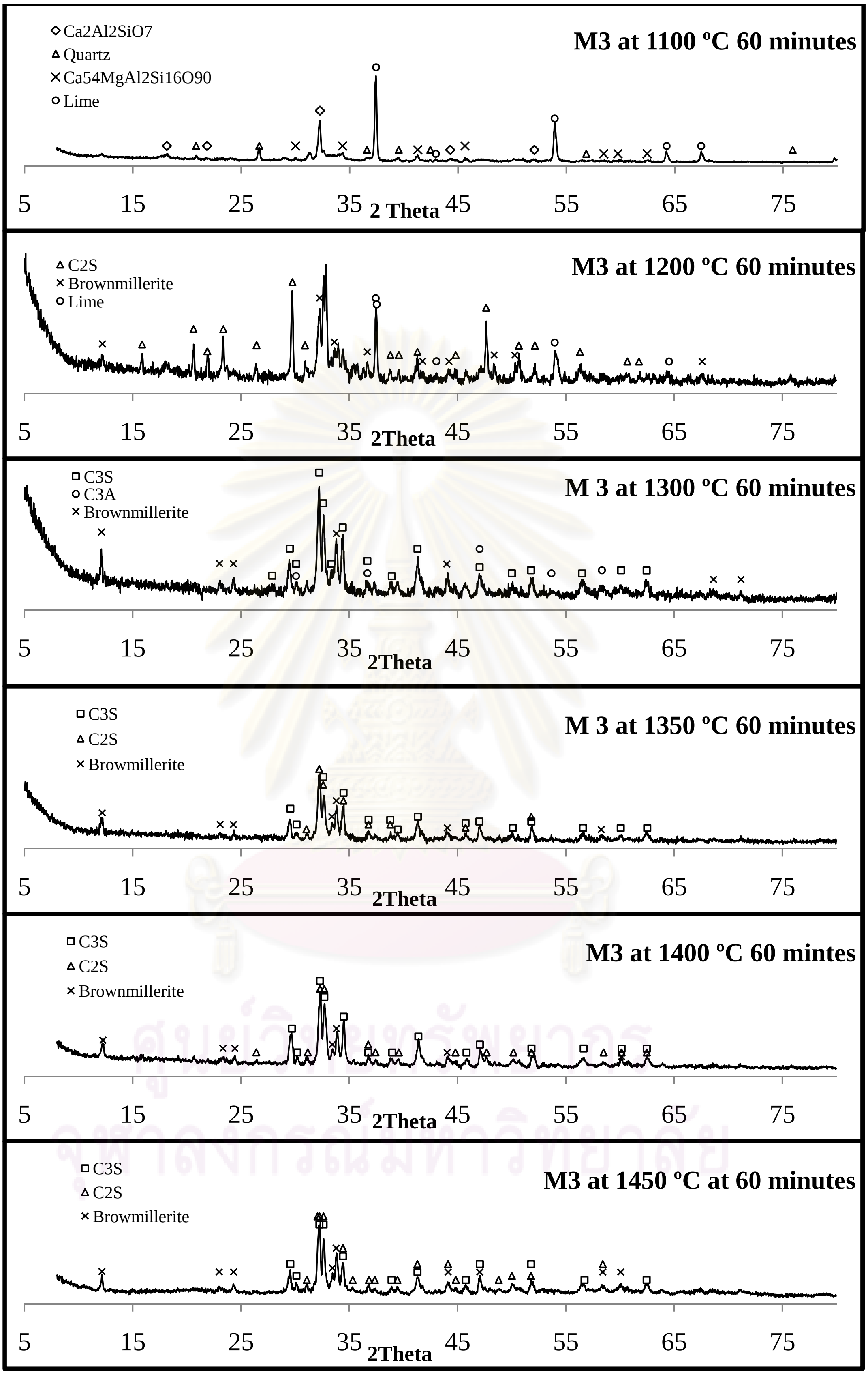


Figure 4.16 X-ray diffraction of clinker sample with 3% by weight of grinding sludge

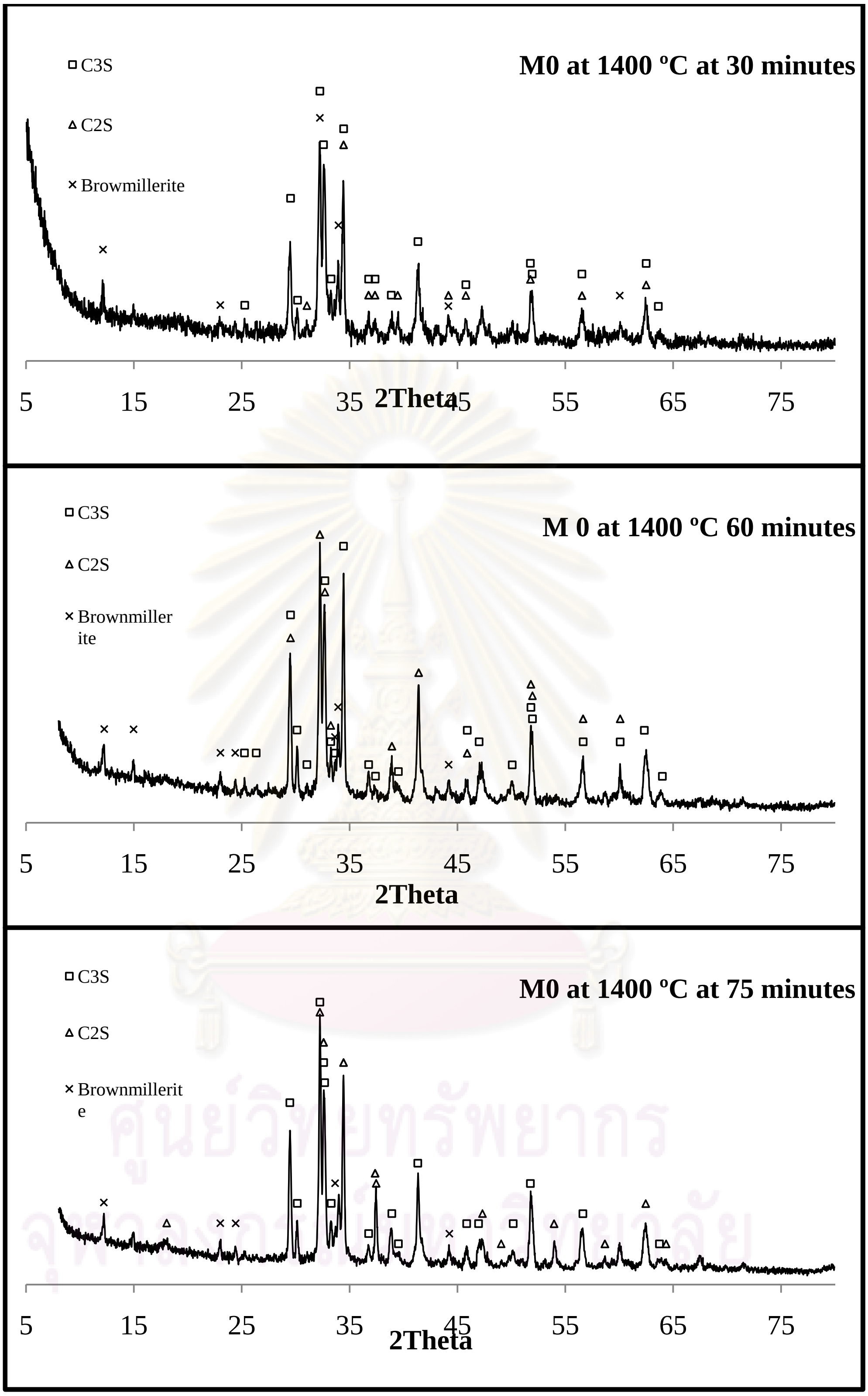


Figure 4.17 X-ray diffraction of clinker sample without grinding sludge at different burning time

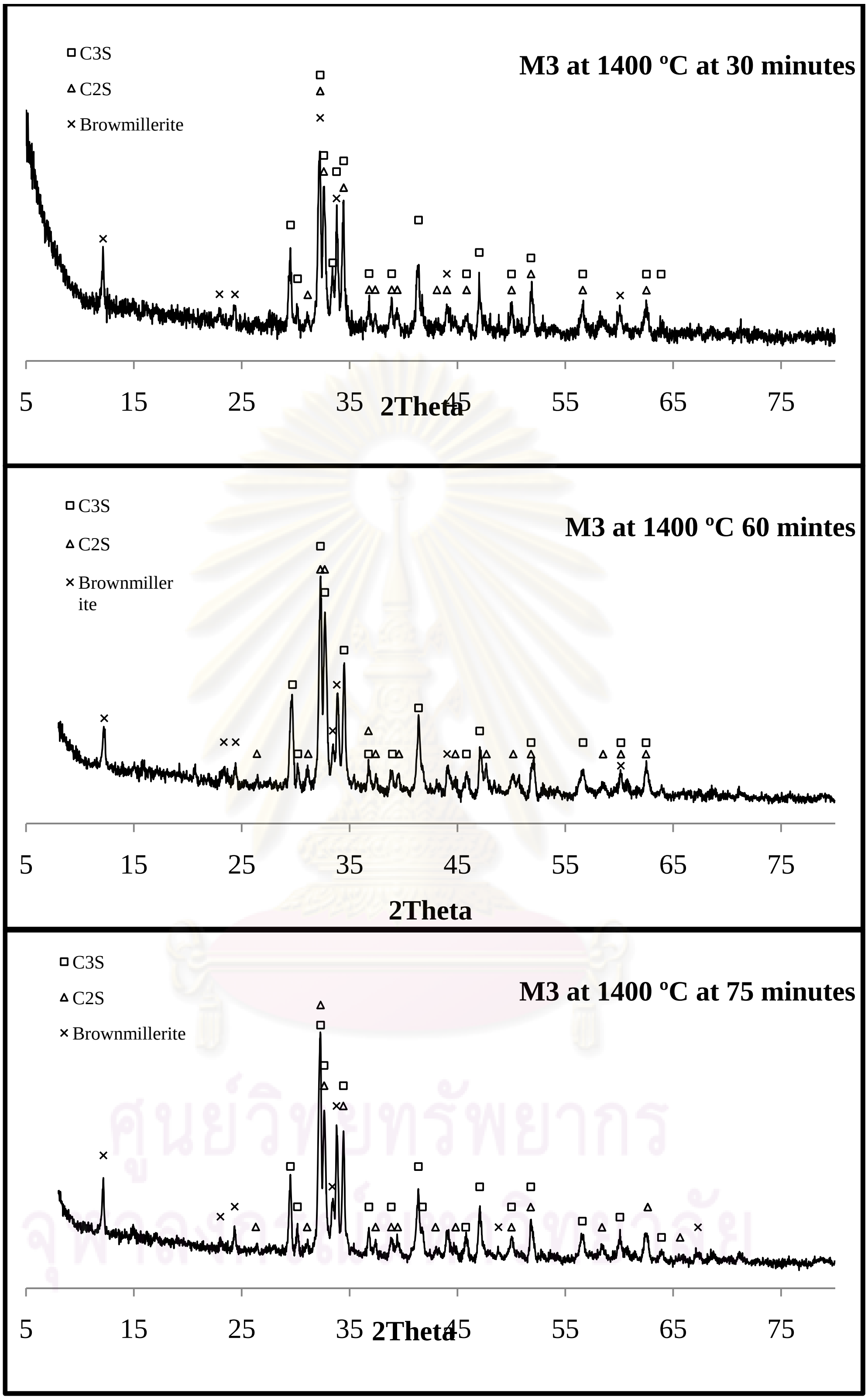


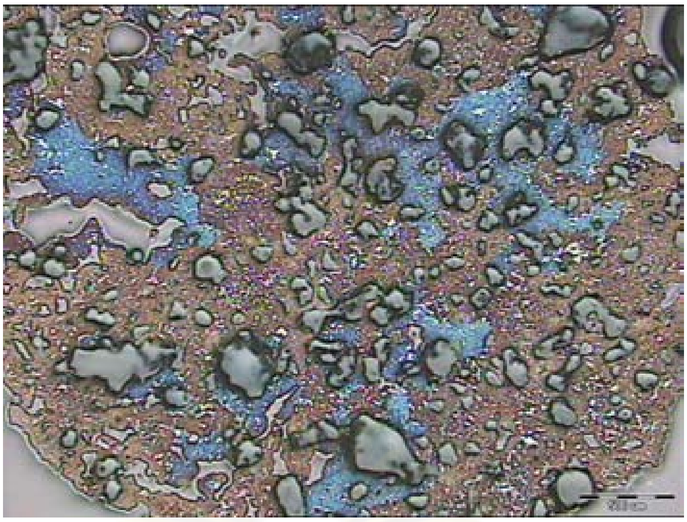
Figure 4.18 X-ray diffraction of clinker sample with 3% of grinding sludge at different burning times

4.2.6 Effect of grinding sludge on microstructure by optical microscope

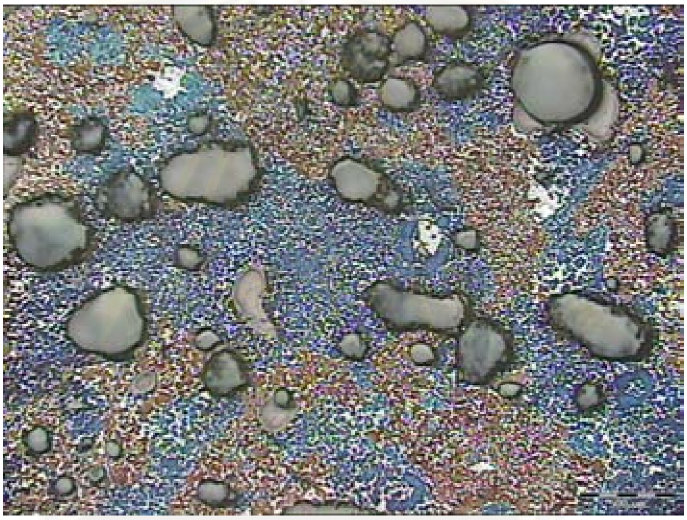
Clinker microstructure was examined by optical microscopy in polished sections. The utilization of grinding sludge as alternative raw material in the clinker burning did not seem to affect its microstructure and the formation of its characteristics mineralogical phases. The synthesized PC clinker of M0 and M3 were compared with the commercial PC clinker. They were displayed on Figure 4.19 to Figure 4.21. The M0, M3, and commercial PC clinker were examined at 5X, 50X and 100X. The magnification at 5X showed the surface of samples. The distributions of free lime in synthesized PC clinker were less than the commercial Portland cement clinker and the free lime of synthesized PC clinker is higher than the commercial PC clinker. The belite is blue color oval shape and the alite is the brownish color and hexagonal shape. According to 50X, the color of belite in M0 and M3 is more than the commercial PC clinker. The belite size of M0 was same as the commercial PC clinker, but the belite size of M3 was bigger than M0 and the commercial PC clinker. The modification at 100X was applied to investigate the C_3S or alite. The C_3S color of M0 and M3 is darker than the commercial PC clinker but the alite of M3 is smaller than the commercial PC clinker. Both of M0 and M3 appeared the secondary belite on alite.

4.2.7 Effect of grinding sludge on microstructure by scanning electron microscope with energy dispersive spectroscopy (SEM/EDS)

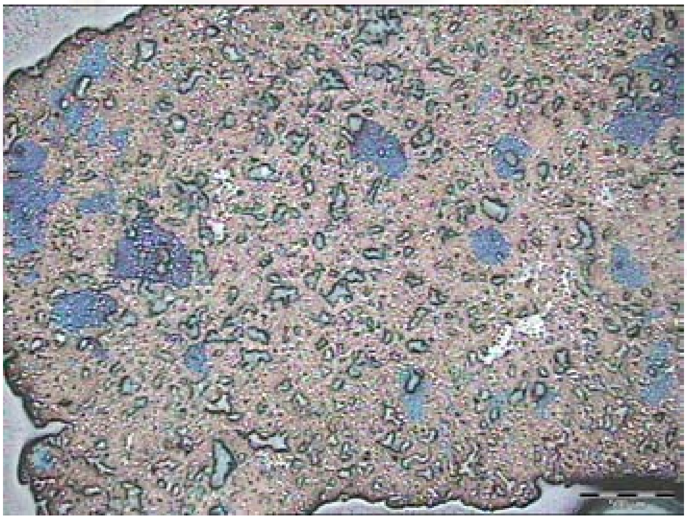
In order to comfirm the optical microscope results, the clinker samples were investigated by SEM/EDS. Figure 4.22 showed the surface of M0 and found the C_2S and other element such as Fe, Al, K and Mg. Figure 4.22 showed that the shape of C_3S releated to the optical microscope and EDS analysis comfrimed that the proportion of Ca and Si approximately equals 3:1. Surprisingly, C_4AF coat on the C_3S surface in Figure 4.24. It concluded that the C_4AF perfer to stick with C_3S while the foreign element tended to agglomerate on C_2S.



(a) 5X of M0

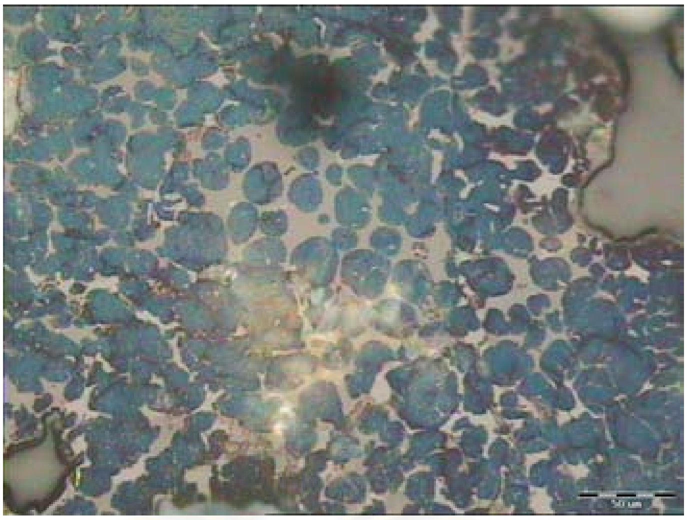


(b) 5X of M3

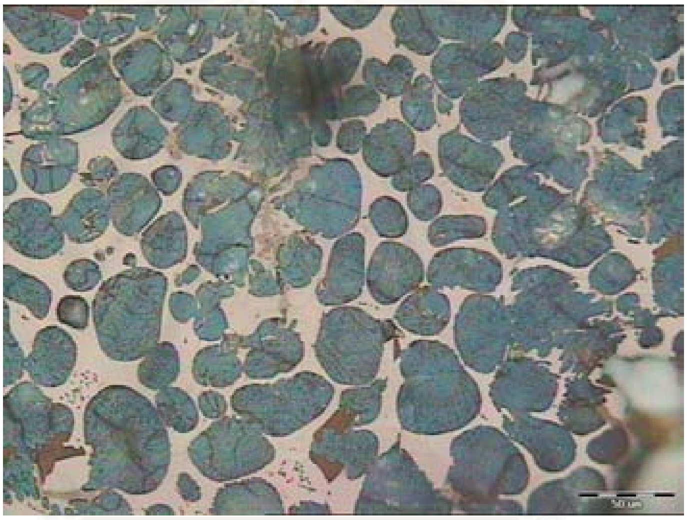


(c) 5X of Comercial PC clinker

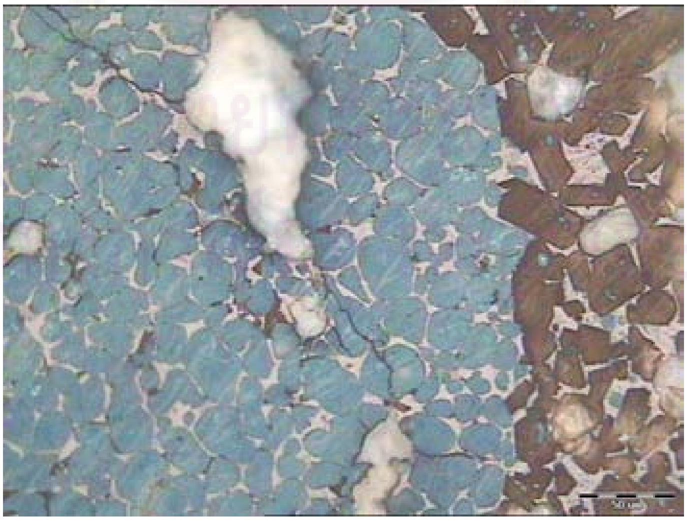
Figure 4.19 Optical microscope examinations of PC clinker at 5X



(a) 50X of M0

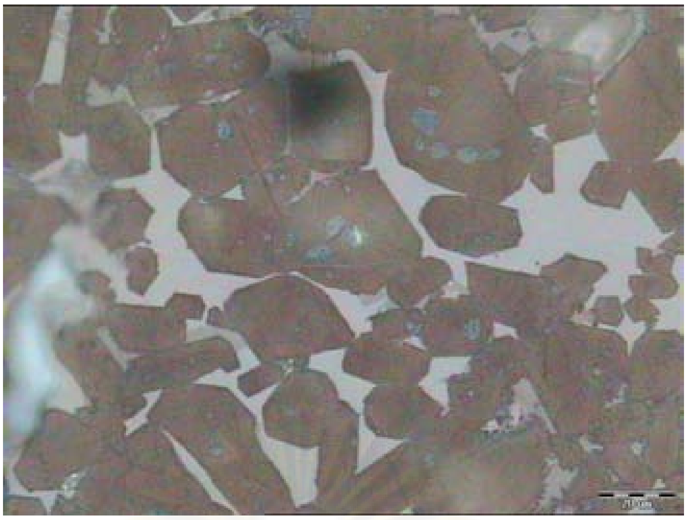


(b) 50X of M3

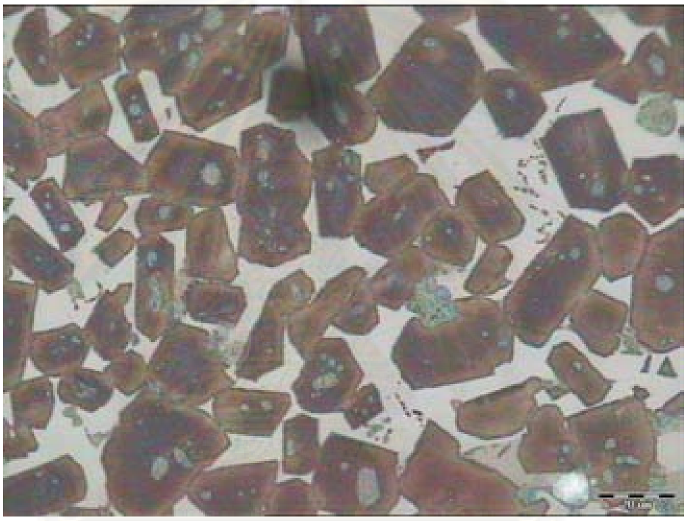


(c) 50X of Comercial PC clinker

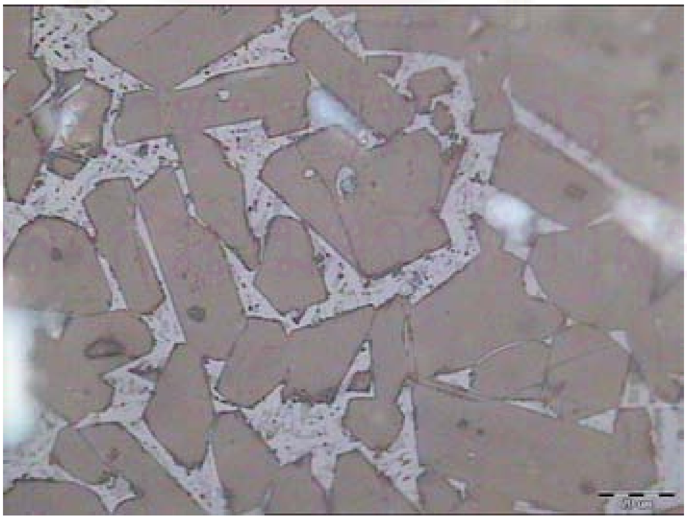
Figure 4.20 Optical microscope examinations of PC clinker at 50X



(a) 100X of M0



(b) 100X of M3



(c) 100X of Comercial PC clinker

Figure 4.21 Optical microscope examinations of PC clinker at 100X

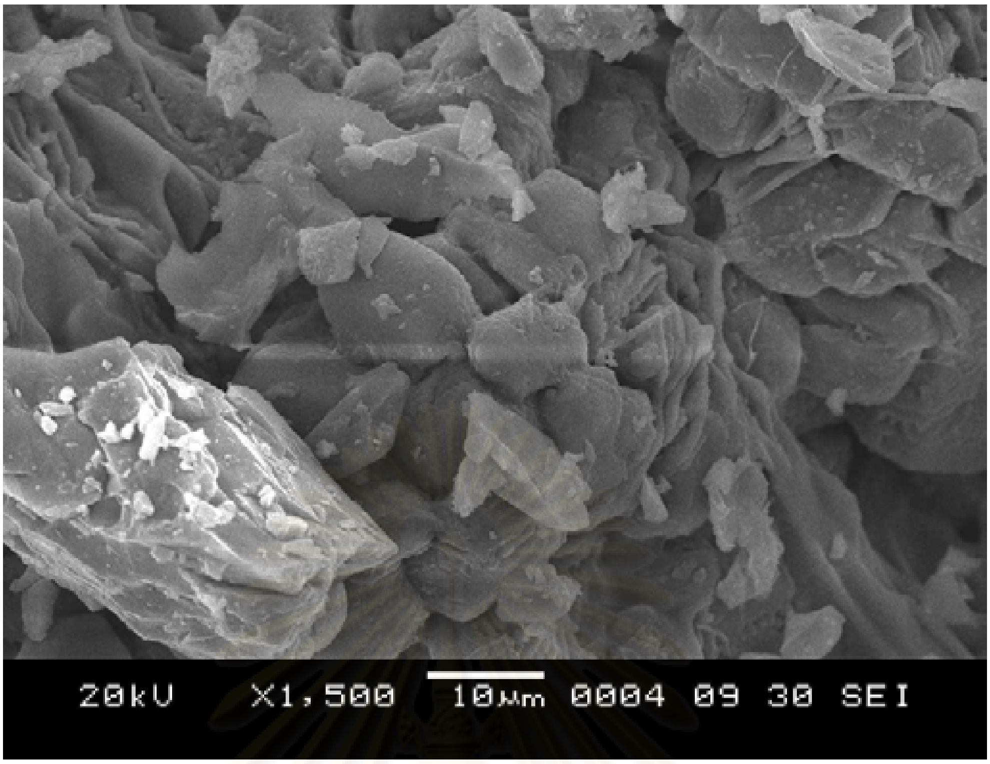


Figure 4.22 C_2S in M0

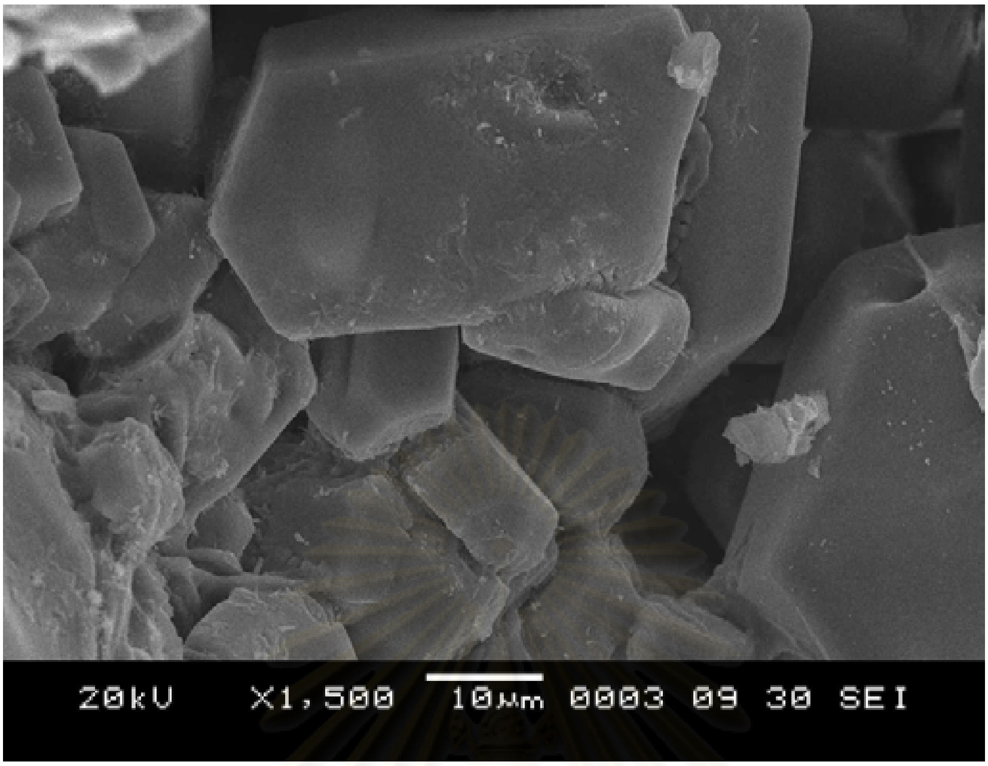


Figure 4.23 C_3S in M1

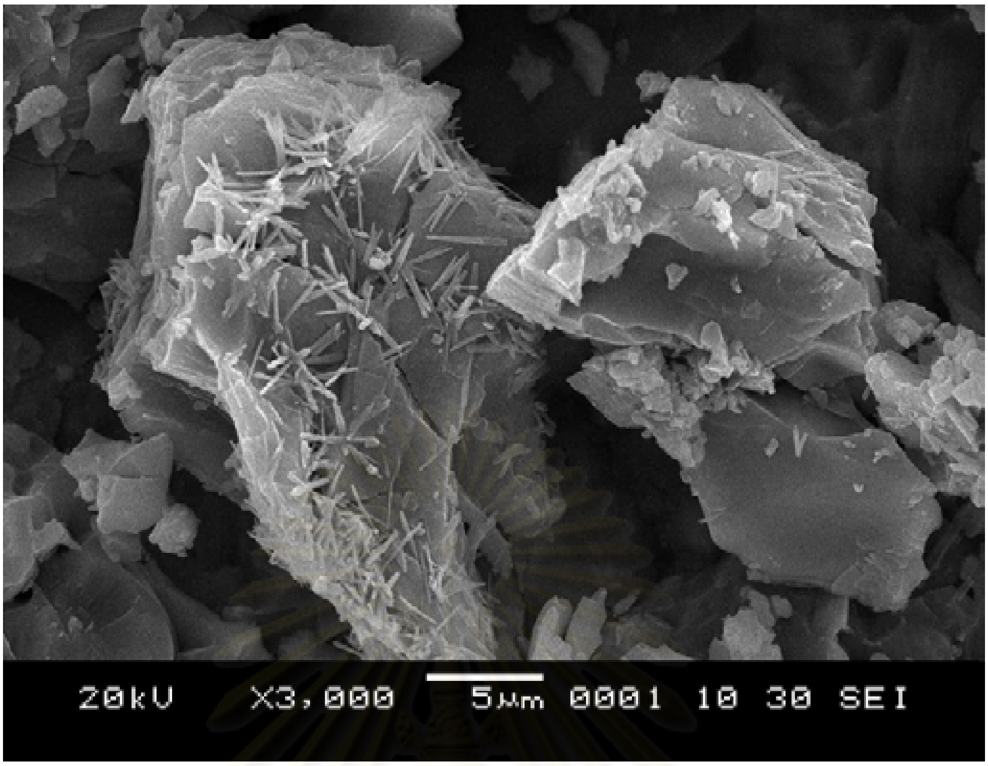


Figure 4.24 C_4AF in M3

4.2.8 Incorporation of heavy metal in clinker

The incorporation percentages of the foreign elements or heavy metals such as Cd, Cr, Cu, Ni, Pb, V and Zn were obtained by comparing the total heavy metal analyses of the raw materials and the synthesized Portland cement clinkers. The results are provided in Table 4.6.The range of incorporation degree of Cd, Cr, Cu, Ni, Pb and Zn in Portland cement clinker were 50-52%, 88-92%, 92-96%, 92-96%, 40-56% and 77-85%, respectively. The incorporation degree of Cd found for the test in the synthesized PC clinker agrees with Espinosa (2000) and Barros (2004), which are roughly 51%. The incorporation degree of Cr suggest with Kolovos (2002), which are approximately 99%. The incorporation degree of Cu was same as Ract (2003). The incorporation degree of Ni was similar to Espinosa and Tenorio (2000). The Pb incorporation degree found in this work was approximately 48%, which agree with Barros's results (2004). Barros found a Pb retention ratio of 50%, when studying a system with no chlorine. The incorporation degree of Zn was roughly 76 %. This result agrees with the results of Barros, Tenorio and Espinosa (2004).

Table 4.6 Incorporation (%) of Cd, Cr, Cu, Ni, Pb, V and Zn in clinker

Synthesized PC clinker at 1400° C 60 minutes	Incorporation degree of heavy metal,%					
	Cd	Cr	Cu	Ni	Pb	Zn
M0	50.07	92.14	92.38	92.38	48.22	76.75
M1	50.64	90.77	95.54	95.54	40.09	78.33
M2	51.32	89.87	96.23	96.23	47.99	81.44
M3	52.08	88.79	96.55	96.55	56.02	84.54

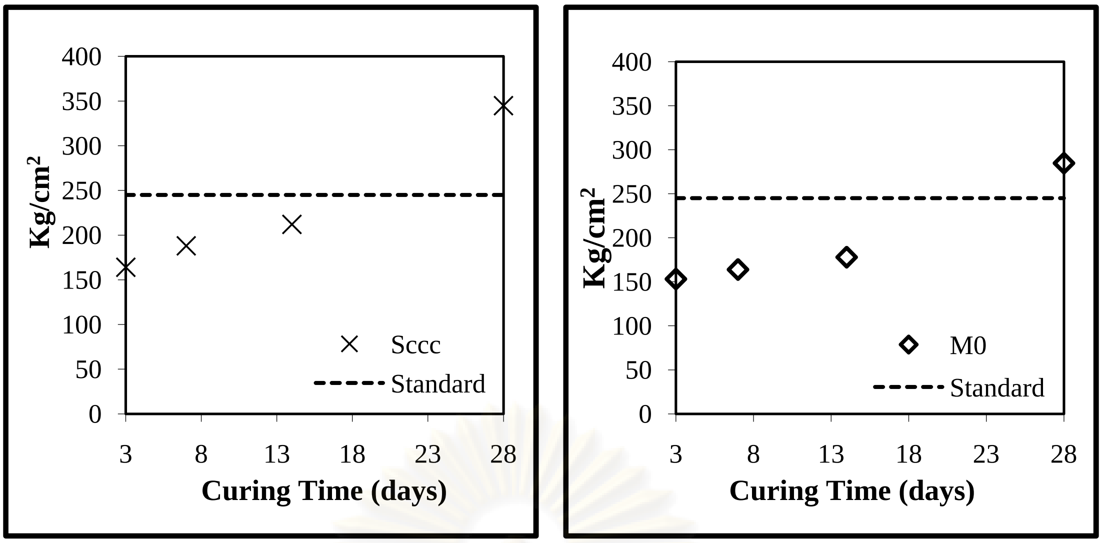
4.3 Leaching of heavy metals from co-processed cement with grinding sludge

According to section 4.2, it concluded that the optimal burning temperature and time were utilized at 1400°C with 60 minutes. In addition, the maximum replacement of grinding sludge was 2 % by weight.

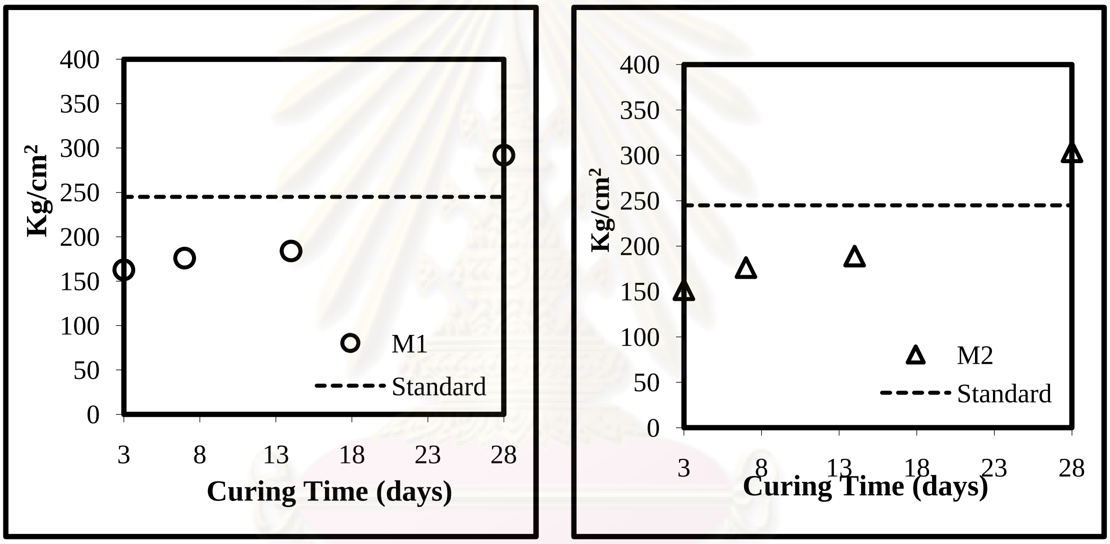
4.3.1 Compressive strength and blain test

The synthesized Pc clinker such as M0, M1 and M2 were grounded with 5 % by weight of gypsum. After that, the samples were measured Blaine fineness. The particle size or fineness of cement in cm^2/g or m^2/kg, usually determined from air permeability tests using a device known as a Blaine permeanmeter. Fineness affects the hydration rate or setting time and the requirements for the amounts of water, retarder and dispersant. The standard value controlled at 3500±100 cm^2/g for ordinary Portland cement type I. The results of Blaine test were given in Figure 4.26. They found that all of results were approximately 3450 cm^2/g. the utilization of grinding sludge did not impact on grinding ability of clinker.

The ground synthesized PC clinker was made the mortar sample by mixing cement to sand ratio at 1/2.75 and a water-cement ratio at 0.485. Then, the samples were cured at 3, 7, 14 and 28 days before compressive strength testing. The compressive strength results were given on Figure 4.25. This testing used the cement from Siam City Cement Company as reference sample (SCCC). It indicated that the compressive strength of SCCC was higher than M1, M2, and M3 at 28 curing days and all mortar samples passed the Thai regulatory standard value at 245 Kg/cm^3. The reason might be that the electric furnace is unfeasible to create a fully stirred circumstance as the rotary kiln. Thus, the contact of raw mix particle was not enough to complete the solid state reaction for the formation of cement product in the burning process or calcination. Therefore, the formation of strength development materials such as calcium silicate is retard (Shin, el at., 2003). The utilization of grinding sludge as alternative raw materials did not impact the cement property especially strength development.



(a) SCCC (b) M0



(c) M1 (d) M2

Figure 4.25 Compressive strength of Mortar (a) SCCC (b) M0 (c) M1 (d) M2

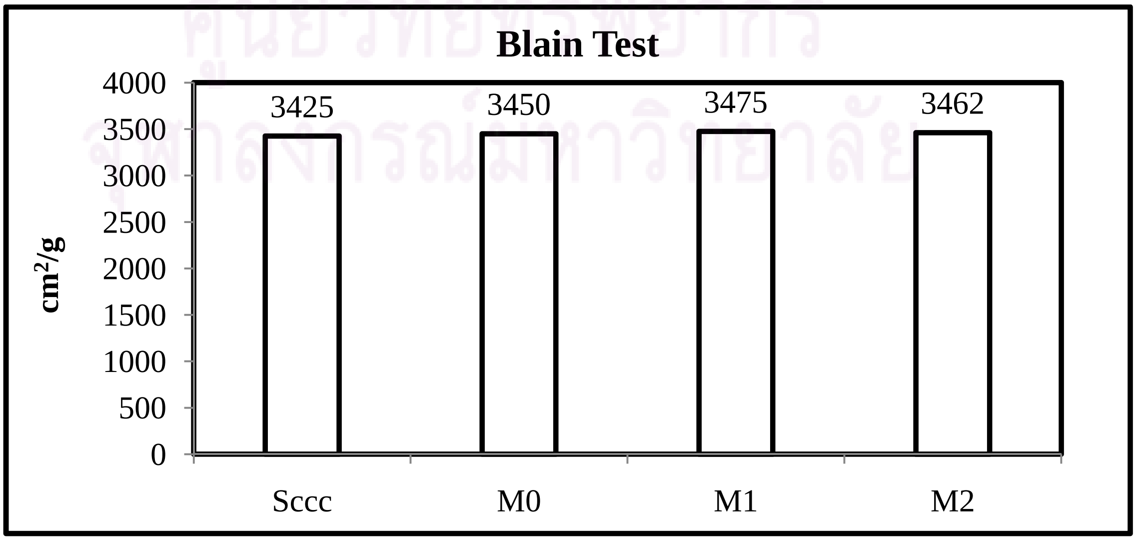


Figure 4.26 Blain Test of synthesized PC cement

4.3.2 Leaching of heavy metals from PC clinker and mortar by regulatory leaching test

The leaching tests were performed according to Thailand regulatory and US regulatory. The Thailand regulatory was enacted by department of industry work (DIW, 2004). It was called wet extraction test (WET). The US EPA was the TCLP method. The main acid leaching solution was used citric acid at pH 5 while the US EPA was employed acetic acid at pH 2.88. The WET and TCLP were applied with synthesized PC clinker and mortar in order to confirm the stability of heavy metals in co-processed cement product and apply the leaching experiment as environmental risk tool.

The WET results of synthesized PC clinker and mortar were given in Table 4.7 and the TCLP results were displayed in Table 4.8. The interesting heavy metals in this section were only Thailand’s hazardous heavy metals such as Cd, Cr, Cu, Ni, Pb, V, and Zn. But, there are no regulatory standard for Cu, Ni, V, and Zn in TCLP because these elements were not classified as hazardous element by the US EPA. Both WET and TCLP results were found that the release of all heavy metals were below the limits for heavy metal concentration. It is confirmed that the heavy metals were really entrapped by the clinker structure (Ract, 2003). The above behaviors were attributed to the high degree of incorporation of heavy metals in the crystal lattice of clinker mineral and delay of their dissolution rate during hydration (Koloves, 2006).

Table 4.7 WET results of synthesized PC clinker and mortar

Heavy metals	**WET**									**STD**
	Clinker					**Mortar**				
	Sccc	**M0**	**M1**	**M2**	**M3**	**Sccc**	**M0**	**M1**	**M2**	
Cd	0.002	0.003	0.004	0.003	0.005	0.617	0.982	0.035	0.736	1
Cr	0.014	0.054	0.351	0.606	1.281	0.399	3.377	1.972	0.625	5
Cu	3.051	2.237	2.440	3.011	4.016	0.433	0.471	0.338	0.396	25
Ni	0.254	0.200	0.549	0.624	0.725	0.816	0.845	0.973	0.737	20
Pb	0.150	0.259	0.188	0.407	0.654	2.033	2.254	1.945	2.017	1000
V	0.404	0.367	0.382	0.414	0.477	0.027	0.003	0.024	0.021	24
Zn	0.077	0.209	0.241	0.255	0.125	1.379	0.950	1.048	1.307	250

Table 4.8 TCLP of synthesized PC clinker and mortar

Heavy metals	TCLP									STD
	Clinker					Mortar				
	Sccc	M0	M1	M2	M3	Sccc	M0	M1	M2	
Cd	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	1
Cr	0.283	0.011	0.044	0.175	0.315	0.216	3.715	2.321	0.498	5
Cu	0.014	0.017	0.015	0.013	0.008	0.004	0.004	0.005	0.004	NA
Ni	0.005	0.007	0.006	0.006	0.008	0.011	0.011	0.008	0.009	NA
Pb	0.274	0.141	0.028	0.193	0.465	0.037	0.035	0.033	0.039	5
V	0.002	0.002	0.002	0.002	0.002	0.005	0.002	0.003	0.003	NA
Zn	0.019	0.017	0.027	0.028	0.029	0.063	0.036	0.031	0.040	NA

4.3.3 Heavy metals speciation in synthesized PC clinker, cement paste and mortar by sequential extraction procedure

The principle of sequential chemical extraction methods is that various chemical aqueous solutions are applied successively to a sample, dissolving the components of the sample matrix in sequential order. Ideally, a reagent should liberate all the metals from a particular matrix's component (i.e. exchangeable, carbonate, etc.), and should not affect the metals in other components. However, it is generally recognized that the partitioning of metals obtained by such procedures is always operationally defined as it is affected by many experimental factors especially the chemical composition of the sample matrix.

The sequential extraction results were expressed as the percentages of heavy metals in each step of the sequential extraction procedures of the two types of mortar. Figure 4.27 through figure 4.29 presented the fractions of heavy metals mobilized under different environmental conditions (Fraction1 for exchangeable, Fraction 2 for bounding to carbonates/specifically absorbed, Fraction 3 for bounding to iron and manganese oxides, Fraction 4 for bounding to organic matter/sulfide, and Fraction 5 for residual).

The distribution patterns of the fraction are different from element to element. This research focused on the difference of the distribution patterns of heavy metals in the three phases of cement product including clinker, cement paste, and mortar. The interesting heavy metals in this part were Cd, Cr, Mn, and Ni. The Cd, Cr, Mn, and Ni had high amount in grinding sludge. They can be seen that the release potentials of heavy metals were obviously greater than in clinker.

First, the heavy metals, which preferred to release on the fraction 1, is the exchangeable element or easily released at neutral condition (pH between 6 and 7). These heavy metals must be concern when they contained in the materials. It can contaminate into environment. Second, the heavy metals, which love releasing into fraction 2, are formed with the carbonate group. Generally, the heavy metals in carbonate form did not dissolve in water except Ba, Co, Ni, and Zn. Third, the heavy metals can easily dissolve in fraction 3, which bounding to iron and manganese oxides in materials. The iron oxide is one of the main chemical compounds in cement product. Generally, the heavy metals like to combine with iron oxide or silica oxide in cement product. Fourth, the fraction 4 was for the heavy metals bind with organic matter/sulfide. The cement production employed the high temperature in production process. It rarely found organic compound in cement product. The sulfide in cement can change only from $CaSO_4$, which blend with clinker for retard hydration reaction. Finally, the heavy metals in the residual fraction or fraction 5 must associate with silica. The heavy meats in this fraction should be bound with silica oxide and hardly release into environment because the silica compound is the strongest bond in cement.

4.3.3.1 Cadmium

About 90% of the total Cd in synthesized PC clinker was connected to the residual fraction. Most of total Cd in cement paste and mortar were associated with the residual fraction. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cd in M2 clinker sample were average 1.0%, 1.6%, 1.5%, and 6.4%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cd in M2 cement paste sample were average 0.1%, 0.3%, 0.2%, and 0.5%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cd in M2 mortar sample were average 0.1%, 0.1%, 0.3%, and 0.4%, respectively. The amount of Cd in each fraction followed the order of residual > iron and manganese oxides > carbonates > organic matter/sulfide > exchangeable. The results indicated that Cd was incorporated into clinker structure; the hydration reaction supported the encapsulation of Cd into CSH phase. The results supported the results of regulatory leaching experiments.

4.3.3.2 Chromium

Almost 88% of the total Cr in synthesized PC clinker and about 95% of the total in cement paste and mortar were combined to the residual fraction. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cr in M2 clinker sample were average 3.1%, 2.6%, 2.0%, and 5.0%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cr in M2 cement paste sample were average 0.1%, 0.06%, 2.3%, and 0.1%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Cr in M2 mortar sample were average 0.7%, 0.6%, 1.1%, and 2.0%, respectively. The amount of Cd in each fraction followed the order of residual > organic matter/sulfide > carbonates > iron and manganese oxides > exchangeable.

4.3.3.3 Manganese

The total of Mn in synthesized PC clinker, cement paste, and mortar were join into residual fraction approximately 80%, 70%, and 84%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Mn in M2 clinker sample were average 0.1%, 0.01%, 34.5%, and 7.5%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Mn in M2 cement paste sample were average 0.02%, 0.02%, 31.6%, and 0.03%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Mn in M2 mortar sample were average 0.06%, 0.06%, 15.3%, and 1.1%, respectively. The amount of Mn in each fraction followed the order of residual > iron and manganese oxides > organic matter/sulfide > exchangeable > carbonates.

4.3.3.4 Nickel

About 90-95% of the total Ni in synthesized PC clinker, cement paste and mortar were merged with the residual fraction. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Ni in M2 clinker sample were average 0.1%, 1.1%, 1.2%, and 5.3%, respectively. The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Ni in M2 cement paste sample were average 0.1%, 0.3%, 0.5%, and 5.0%, respectively.

The exchangeable, carbonates, iron and manganese oxides, and organic matter/sulfide fractions of Ni in M2 mortar sample were average 0.3%, 0.1%, 0.3%, and 3.7%, respectively. The amount of Ni in each fraction followed the order of residual > organic matter/sulfide > iron and manganese oxides > carbonates > exchangeable.

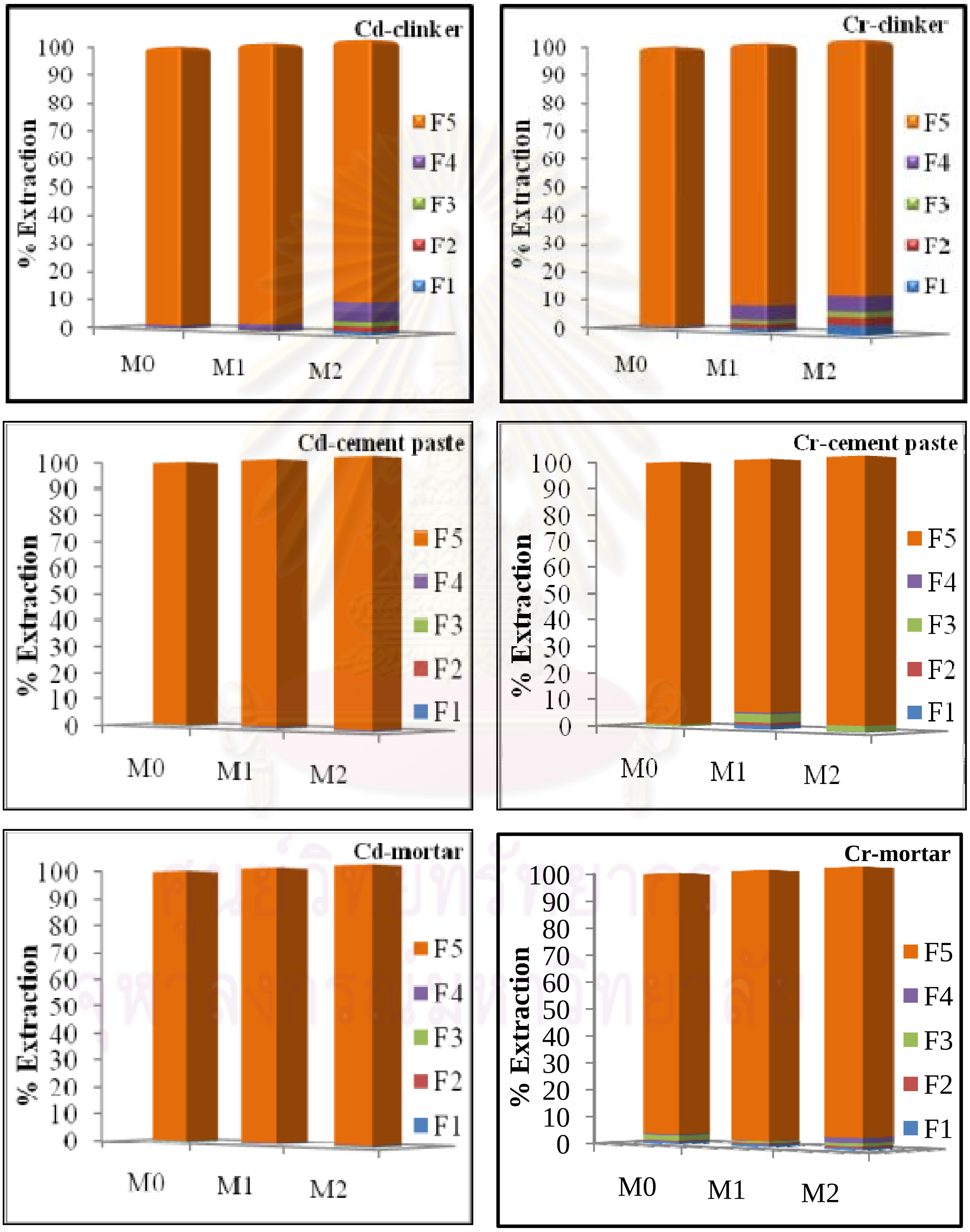


Figure 4.27 Distribution of cadmium and chromium among the clinker, cement paste, and mortar samples

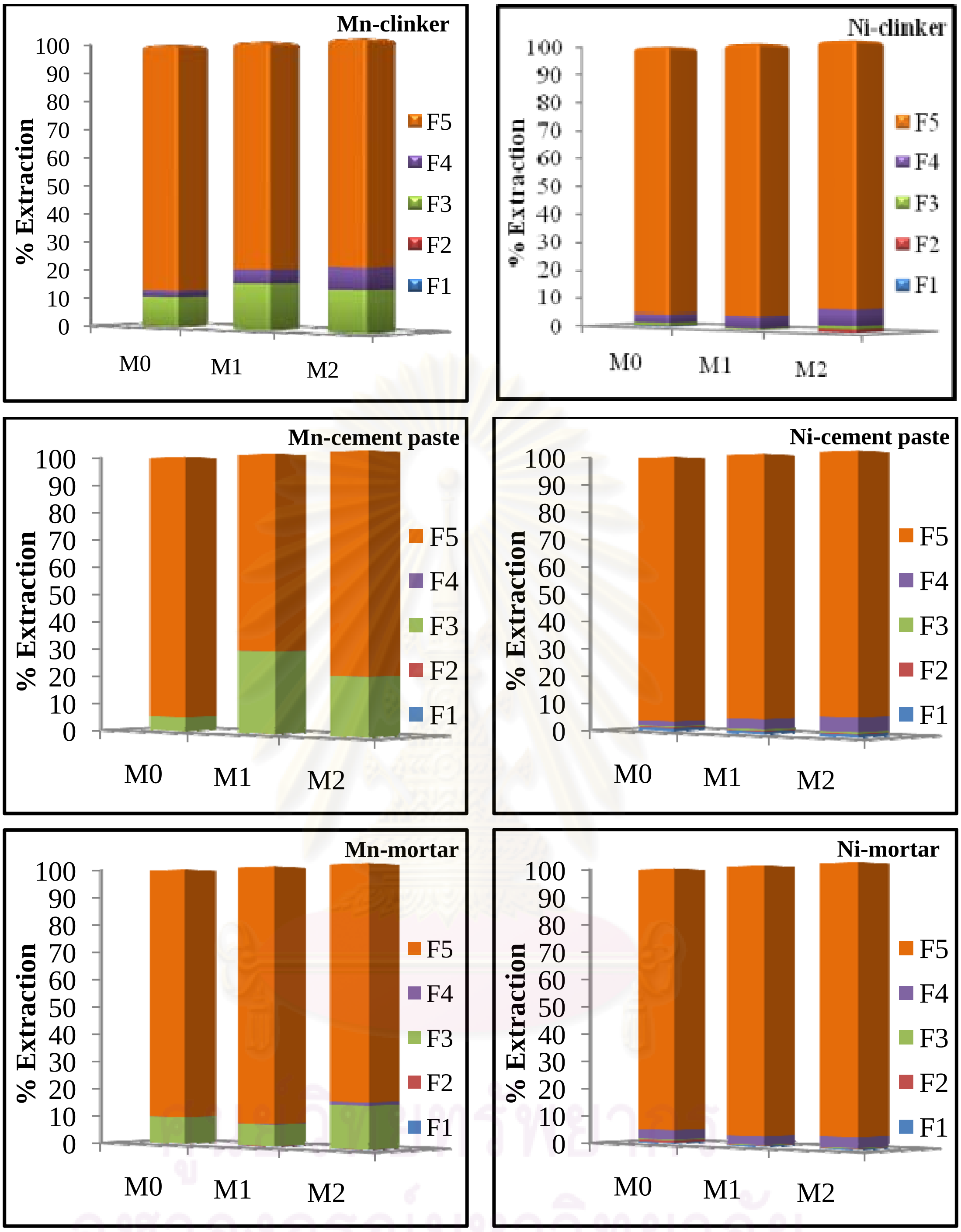


Figure 4.28 Distribution of manganese and nickel among the clinker, cement paste, and mortar sample

4.3.4 Long –term prediction of the leaching behavior of heavy metals from co-processed cement mortar with grinding sludge

This section concerned on the leaching behavior of heavy metals from co-processed cement mortar with grinding sludge. There were three experiments for prediction of the leaching behavior. Pore water test (PW) was good for the case of very soluble species such as alkaline. It gave the initial equilibrium composition of the pore solution and the soluble species maximum mobile fraction (MMF) for leaching. Acid neutralization capacity test (ANC) aimed to study the influence of pH on the leacheability of inorganic constituents from co-processed cement mortar. It predetermined the amount of acid or base to reach to desired end pH values in steady state condition. Monolithic leaching test was based on the tank test NEN 7375 (NNI, 2005). It relates to the determination of the leaching of inorganic components from moulded or monolithic materials using the diffusion test. The purpose of this diffusion test is to simulate the leaching of inorganic components from moulded and monolithic materials under aerobic conditions as a function of time over a period of 64 days. The test determines the nature and properties of the material matrix under investigation by placing a complete sample in a leaching fluid (demineralised, pH neutral water) and replenishing the eluate at specified times. The concentrations of the leached components in the successive eluate fractions are measured. The pH value at which leaching takes place is determined by the material itself. On the basis of the diffusion test results, the leached quantity per unit area can be calculated for each component analyzed. Parameters can be deduced from the development of the release of components over time, including the extent of surface rinsing and the effective diffusion coefficient that can be used to estimate the leaching over longer periods.

This section used the M2 as a representative of sample. The M2 is the highest replacement percent of grinding sludge in the synthesized PC clinker. It assumed that M2 had high concentration of heavy metals. The high concentration of heavy metal in sample can allow easily the prediction leaching behavior.

4.3.4.1 Pore water test (PW)

Figure 4.29 displayed the pH level of solutions in equilibrium with M2. It observed that the pH of M2 was approximately 12.5. It associated with a common pH level in cement materials. The cement materials gave the alkaline pore solutions.

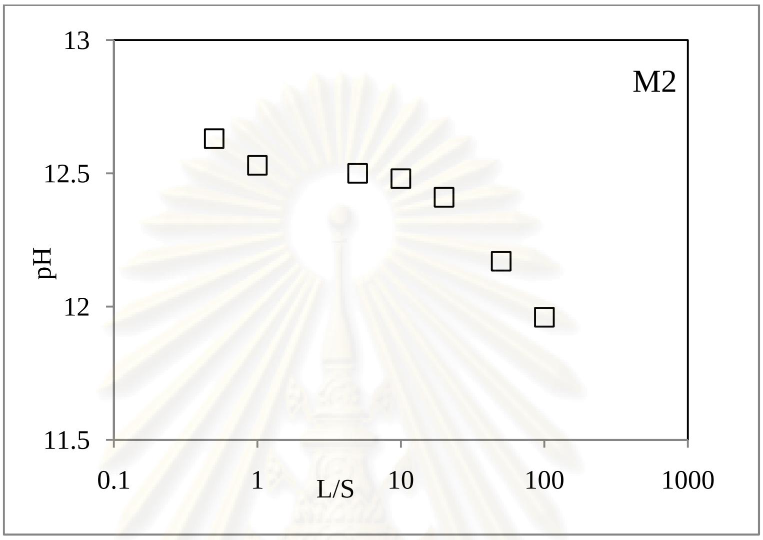


Figure 4.29 pH in the pore solution of M2 (n=5)

A) Alkali metals

Figure 4.30 was showed the concentrations of alkali metals (Group IA) in the pore solution of M2. The representative of alkaline group IA contained potassium (K), Lithium (Li), and Sodium (Na). The alkali metal was classified as soluble group because the element in this group did not precipitate in any reagent. The logarithmic graph between concentration of K, Li, and Na and L/S were linear. The concentration of K, Li, and Na were high at low L/S ratio. It indicated that these elements came from highly soluble phases of the cement materials. It can be assumed that the initial pore water, corresponding to a steady state saturated pore system contains all the available quantity of these elements. These results associated with those of Tiruta-Barna, el at. (2004). The leaching available quantities deduce from this test for the soluble elements were lower than the total content.

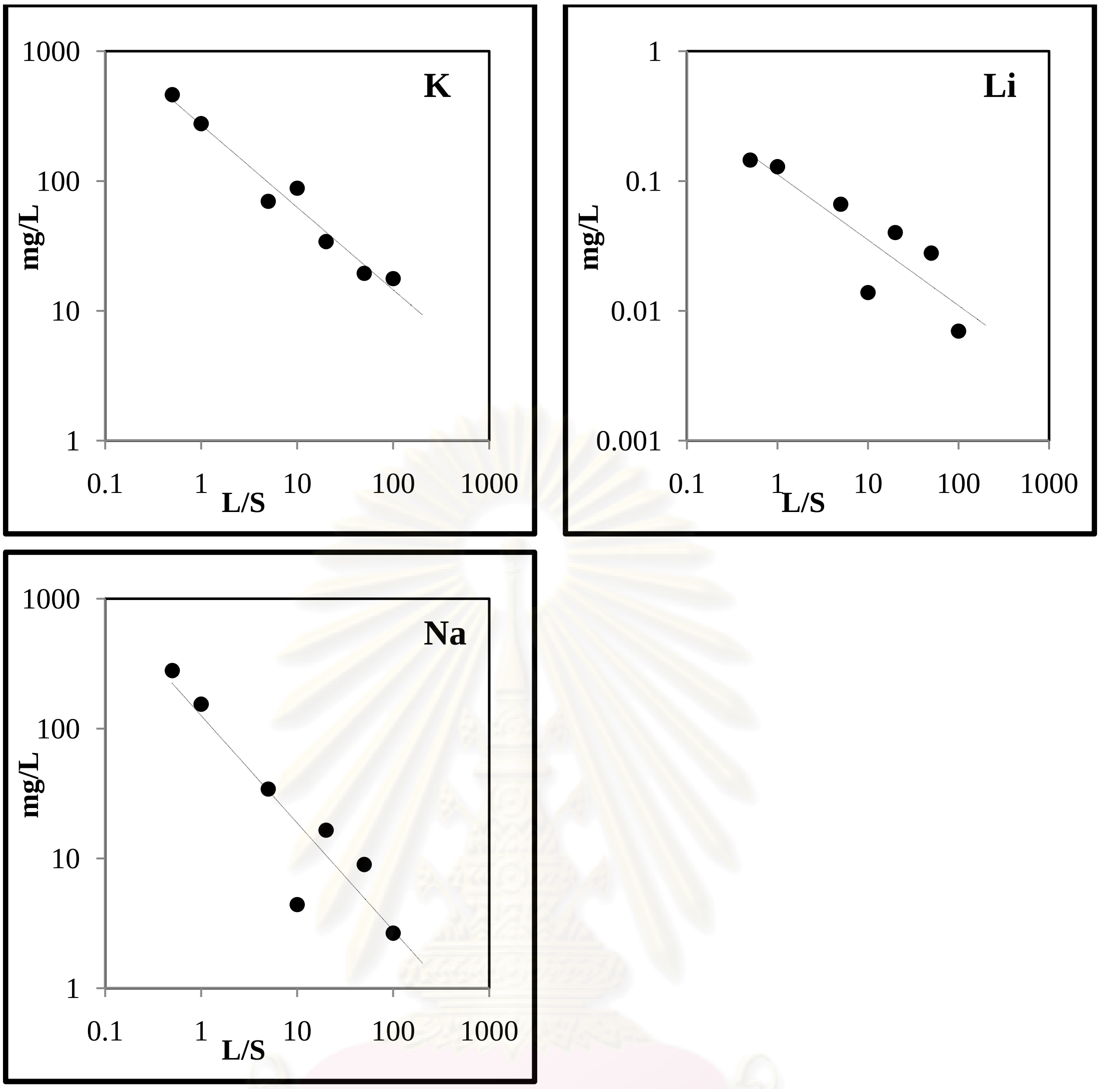


Figure 4.30 Concentrations of alkaline metals (Group IA) in the pore solution of M2 (n=5)

B) Alkaline earth metals

The representative alkaline earth metals were magnesium (Mg) and Calcium (Ca). The result of Mg differed from the results of Ca. Mg graph was similar to that of alkali group. It assumes that the Mg form could be in the soluble compound in cement materials. Nevertheless, Ca is more complex and is mainly determined for the solution pH, by the solubility of the Portlandite from cement mortar. The increasing L/S or dilution influenced a decrease in pH and an increase of Ca solubility. In addition, the decrease of the ionic strength by dilution favored its solubility. The pore water results of Mg and Ca were showed in Figure 4.31.

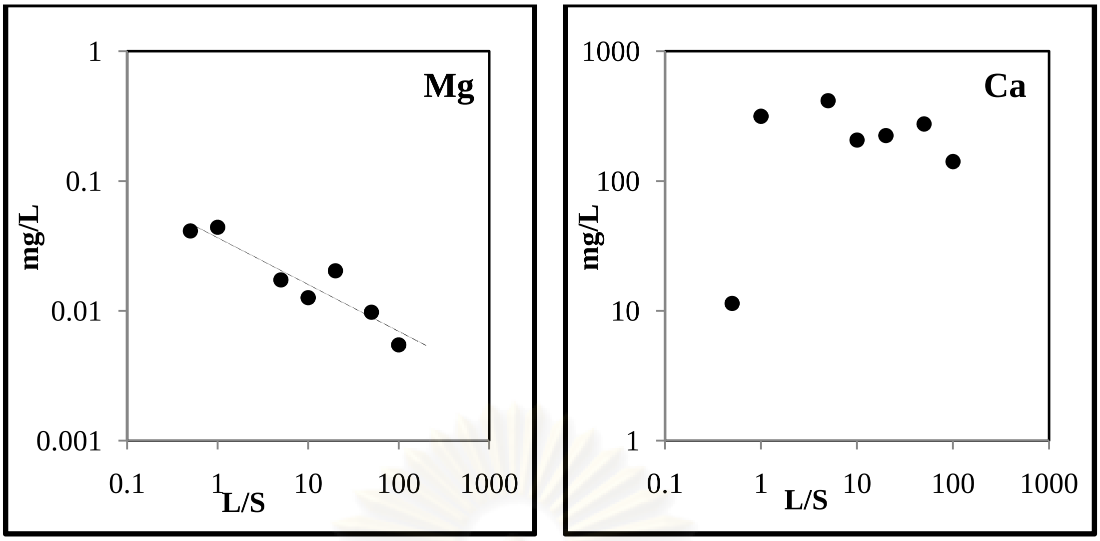


Figure 4.31 Concentrations of alkaline earth metals in the pore solution of M2 (n=5)

C) Transition metals

The pore water results of transition metals were given in Figure 4.32. The increasing of L/S ratio slightly impacted on the release of transition heavy metals. The concentration of transition metals has remained constant. It indicated that the transition metals dissolved into the leaching solution and the saturation in leachant was reached. A possible explanation for this might be that the transition metals tend to complex strongly with cement composition. In addition, the leaching potential of heavy metals in cement product must be less than in neutral pH or high pH state. The pH of DI water was approximately 6 and the pH after testing in Figure 4.29 was nearly 12.5. Therefore, the transition metals were formed in metals hydroxide and dislike to dissolve in neutral pH or base solution.

Finally, the composition of the pore solution for each material may be estimated from the L/S dependent composition of the test solutions at the L/S ratio corresponding to the saturated open porosity. This L/S ratio is evaluated from the Water absorption capacity determined from the Monolithic leaching test.

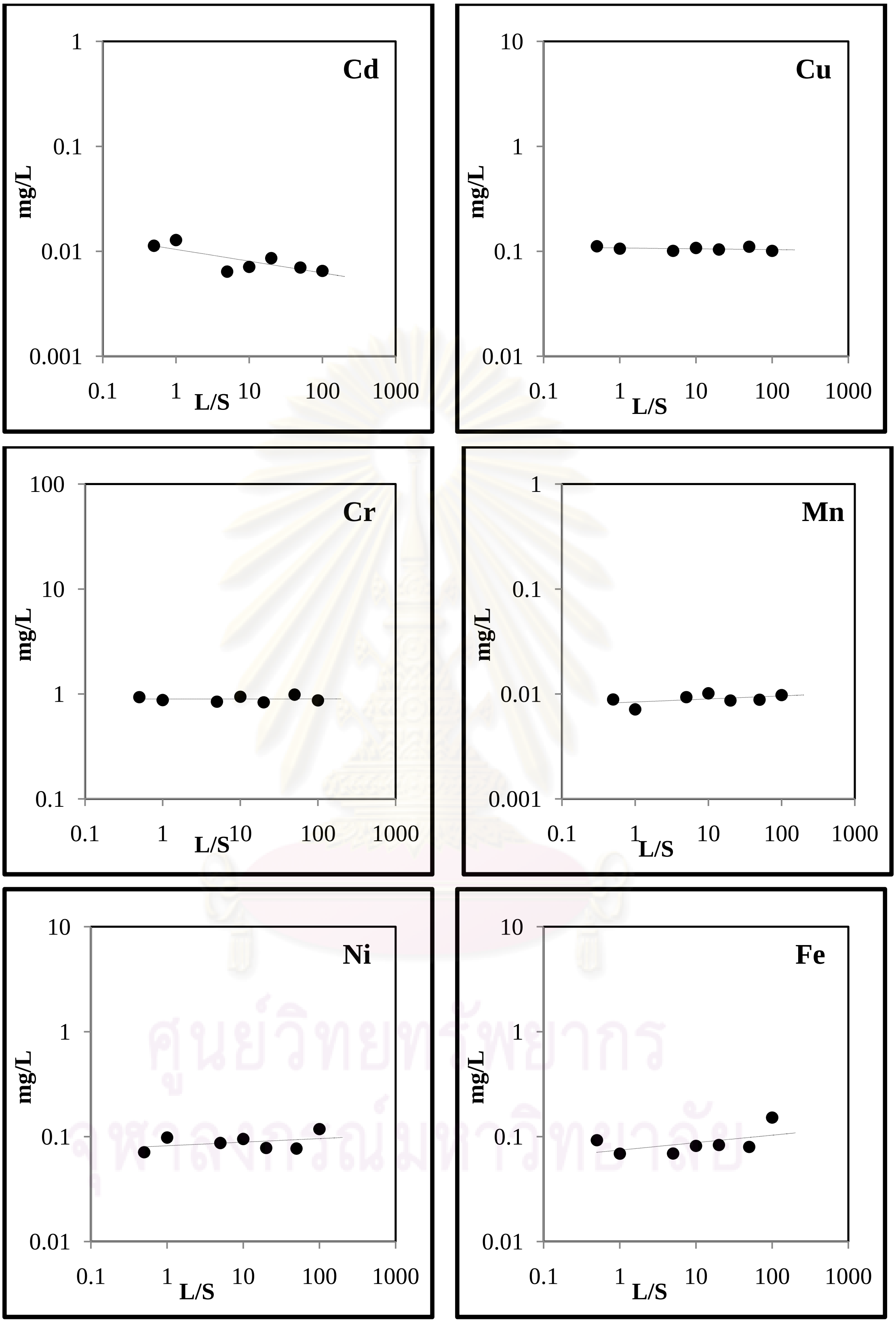


Figure 4.32 Concentrations of Cr, Zn, Mn, Ni and Fe in the pore solution of M2 (n=5)

4.3.4.2 Acid neutralization capacity (ANC) test

The acid neutralization capacity (ANC) results gave the leaching behavior of constituents as a function of pH. The leaching pattern obtained with the ANC test was the results of a combination of the materials-specific chemical factors. The ANC results displayed the buffering capacity in materials. General leaching behavior of three groups of constituents as a function of pH was displayed in Figure 4.33. Cation, anion, and soluble salts have a distinct leach pattern, caused by their chemical speciation and very orders of magnitude as a function of pH.

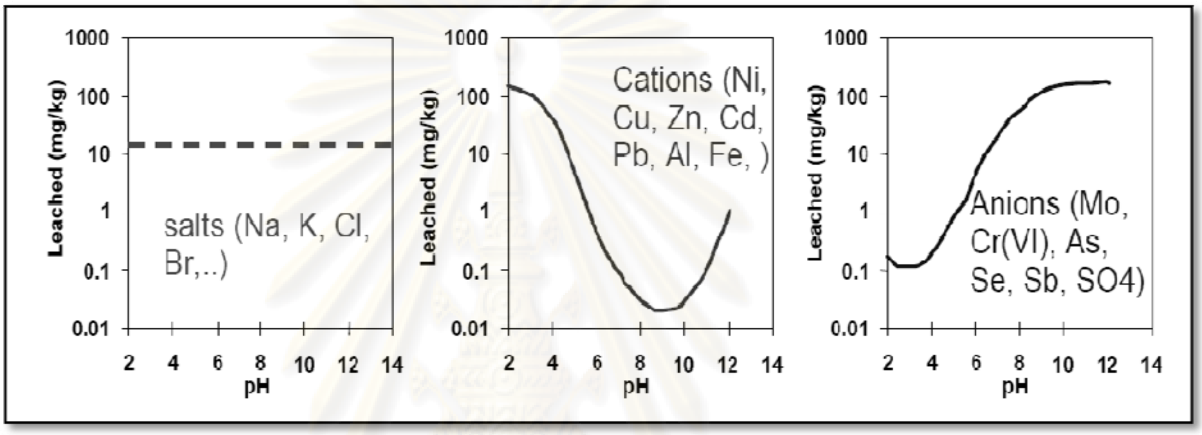


Figure 4.33 Leaching behavior patterns of constituents as a function of pH (van der Sloot and Dijkstra, 2004)

The synthesized PC clinker at 2 % of grinding sludge replacement was used to produce the cement mortar. The cement mortars were cured at 28 days before undergoing ANC test. The results were classified into three patterns including soluble salts, alkaline earth metals, and cation metals.

A) Soluble salts

The ANC of soluble salts in cement motor at 2% of grinding sludge replacement was shown in Figure 4.34. The representative of salts group was Na and K. The pH did not affect the solubility of Na and K. The concentrations of Na and K remained stable. It is interesting to note that the release of salts from co-processed cement did not depend on the pH. The results of Na and K related to the theatrical leaching pattern in Figure 4.33. It agrees with the properties of salts such as high solubility and non- reactivity.

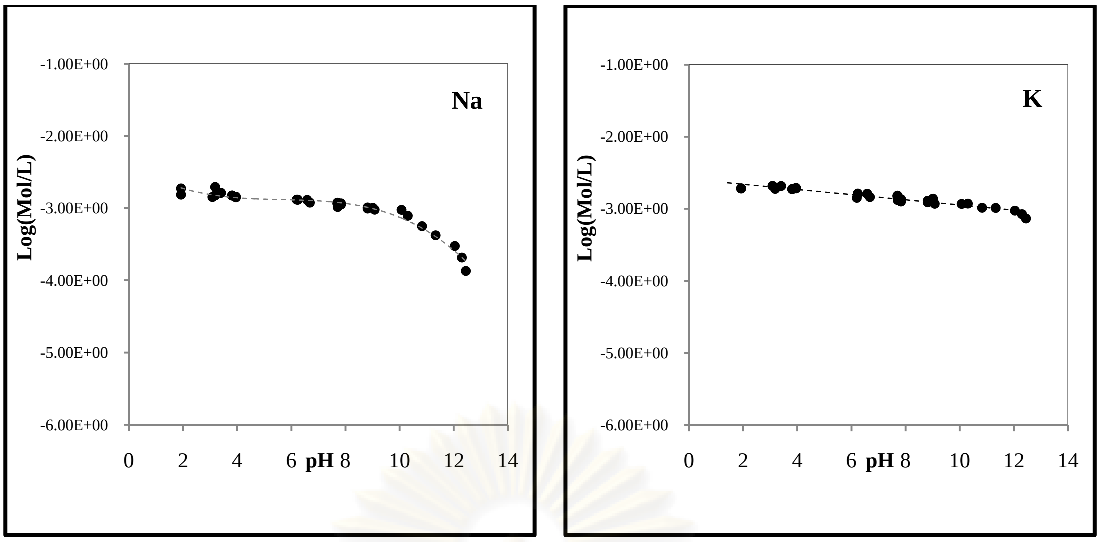


Figure 4.34 Leaching behavior of salts in cement mortar (n=5)

B) Alkaline earth metals

The ANC of alkaline earth metals in cement motor at 2% of grinding sludge replacement was shown in Figure 4.35. The representative of alkaline earth metals was Ca and Mg. Their solubility decreased as pH increased and became negligible for pH > 12. In this region, the alkaline earth metals could form strong alkaline hydroxides. Normally, the alkaline earth metals gave basic alkaline solutions. Moreover, the alkaline earth metals easily released to acid leaching solution and precipitated in alkaline solution.

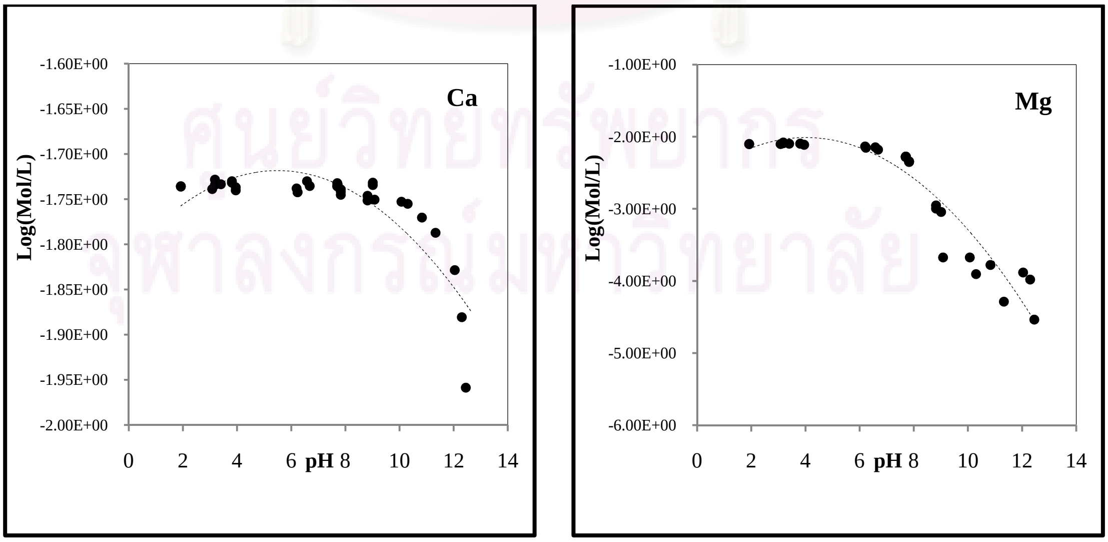


Figure 4.35 Leaching behavior of alkaline earth metals in cement mortar (n=5)

C) Other cations

The ANC of cation metals in cement motor at 2% of grinding sludge replacement was shown in Figure 4.36 and Figure 4.37. The overview results of cation associated with the leaching pattern of cation in Figure 4.33. It was found that the leaching behavior of Zn and Cu slightly differed from the normal leaching pattern. A possible explanation for this might be attributed to the releases of Zn and Cu were the difference in redox potential and salt strength. The solubilization of other cation was strongly dependent on pH. The solubilization of Al and Cu was a minimum in the pH range from 7 to 10. While the solubilization of Ni, Mn, and Zn were a minimum in the pH range from 8 to 12. It was found that a concentration of buffering capacity occurred at low pH (less than 4) according to ANC results. It suggested that the most soluble solid phase containing metals were entirely dissolved in pH < 4. In order to assess the cation metals leaching behavior using a coupled chemical/transport model, it correlated the metals solubilization with pH value by polynomial regression as presented in dash lines.

Moreover, the ANC of Cd and Cr in cement motor at 2% of grinding sludge replacement was shown in Figure 4.36. The solubility of Cd and Cr increased when pH increased. The leaching behavior of cadmium and chromium did not support the theatrical pattern in figure 4.33. The previous study is S/S sample but this research is co-processed sample. These results did agree with the previous study because the sample is a different phase of solid. The Cd and Cr in co-processed cement mortar slightly showed soluble or insoluble in any pH because most of Cd and Cr incorporated into cement particles.

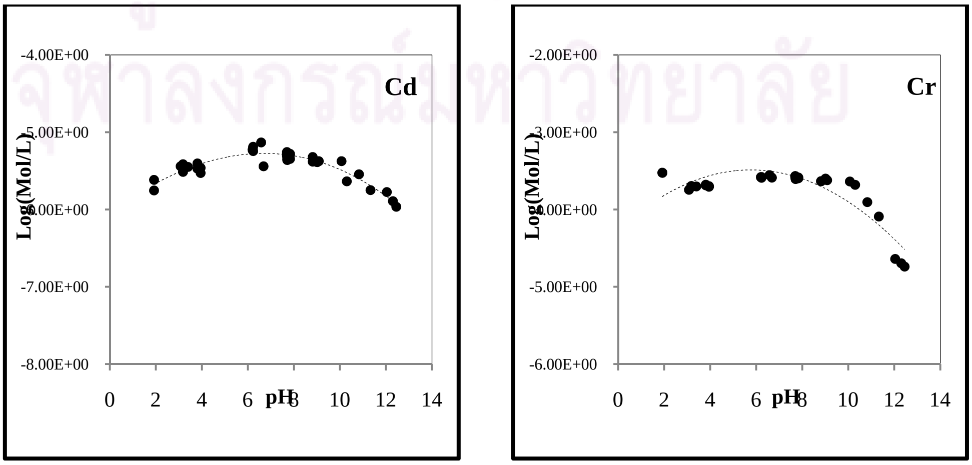


Figure 4.36 Leaching behavior of transition metals in base solution (n=5)

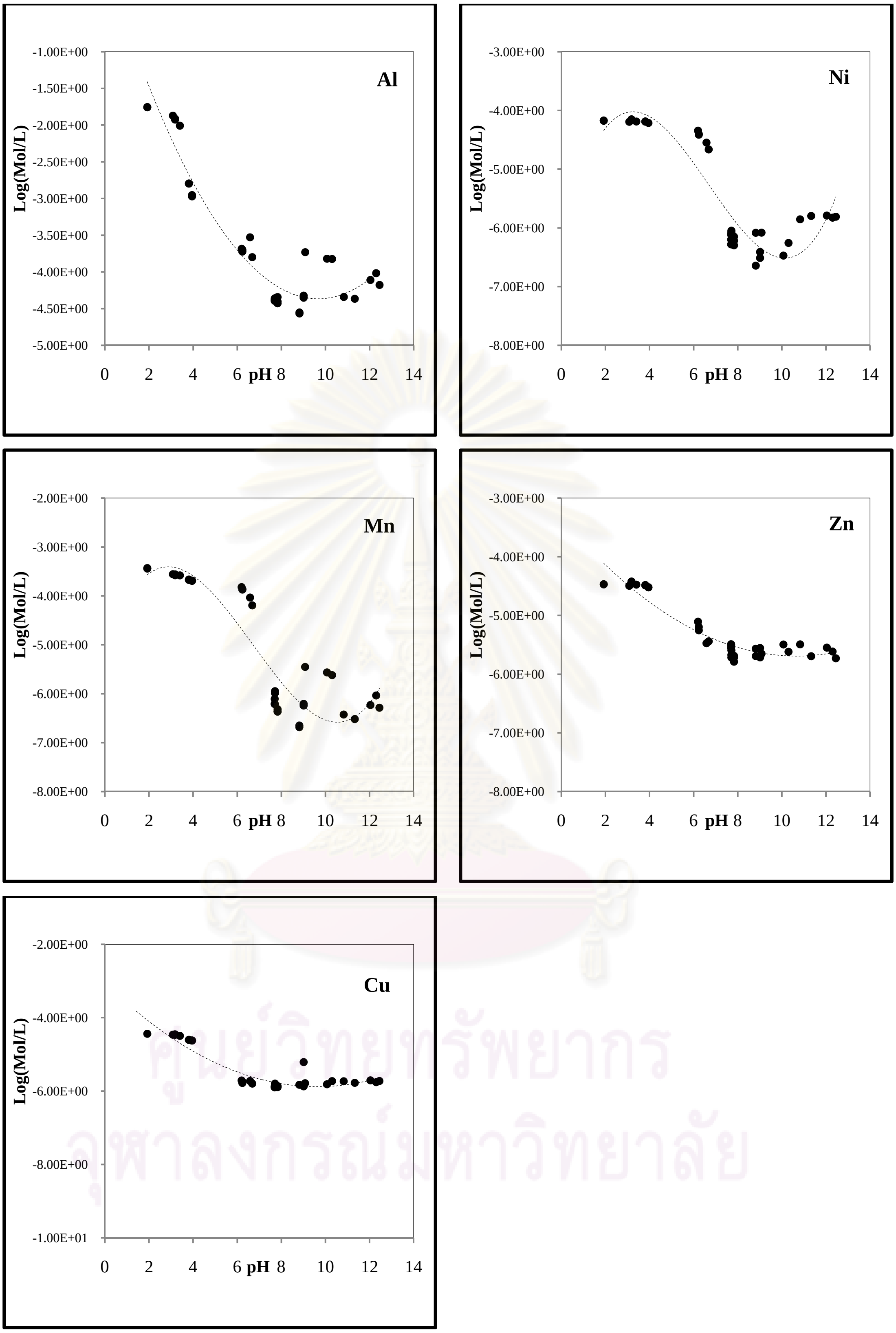


Figure 4.37 Leaching behavior of cation metals in cement mortar (n=5)

4.3.4.3 Monolithic test and mathematic model

The ML test gave the physic-chemical parameters of the eluates at the end of each leaching sequence. The parameter contained the concentration of released species, pH value, etc. The experimental results were presented in released flux and pH. The ML test results were interpreted and compared with those obtained from the mathematic model which described in Section 3.3.2.7. The ML results were plotted in comparison with the mathematic model results. The results from PW and ANC test put into the mathematic model. All of significant parameters for running model were given in Table 4.9 and Table 4.10. The interesting heavy metals in this section were cadmium, chromium, and nickel. In addition, Na and K were interpreted by mathematic model. They were a representative of salt group. The comparison between experimental results and stimulation results of salts and heavy metals were given in Figure 4.39. The predication of leaching behavior was explained. The result of pH of M2 was shown in Figure 4.38. The eluate pH has remained constant during the test, closed to 12. The simulation results were similar to the experimental results. The pH value increased when the time increased. This result may be explained by the fact that some mechanisms occurred and release the hydroxide in the eluate.

The slope of Na and K graph was nearly 0.5. It estimated that the release of salts in cement mortar was controlled by diffusion mechanism at the long term (van der Sloot and Dijkstra, 2004). The depletion was observed at the end of leaching period.

The releases of Ca, Cd, and Cr were controlled by surface wash-off and diffusion mechanism. First, the concentration of Ca, Cd and Cr showed the originated straight line. The straight line below the experiment results reflected the surface wash-off. Surface wash-off is a process that is similar to advection. The term surface wash-off is used to define the (initial) wash-off of soluble materials on the outside of monolithic products. Next, the release of Ca, Cd, and Cr was controlled by diffusion mechanism. After the initial wash-off, diffusion is normally the major transport mechanism in monolithic materials.

The release of Ni looked like Na and K results. It observed that the slope of Ni was nearly 0.5. It can conclude that the release of Ni was controlled by diffusion mechanism.

The diffusion coefficients were obtained by the mathematic model. The diffusion coefficient was a property of constituent in porous materials. The diffusion coefficient gave an idea of chemical release. The high diffusion coefficient value means the release potential of chemical into environment. Table 4.10 reported the diffusion coefficient of salts (Na+K), Ca, Cd, Cr, and Ni. The highest potential release of heavy metal was Ni. The lowest potential release of heavy metals was Cd. The potential risk of constituent in M2 followed Ni > Ca > Cr > Na+K > Cd.

Table 4.9 Physical properties of the materials

Physical parameter	**M2**
Density (g/cm^3)	1.93
Water absorption capacity, WAC (%)	12.74
Total Heavy metals (mg/Kg)	
Na	5745.2
K	260.7
Ca	4021200
Cd	56.3
Cr	396.8
Ni	80.5

Table 4.10 Parameter used in the model application to ML

Application	**M2**		
Porosity of specimen	0.127		
Monolithic eluate exchange surface (m^2)	0.015		
Volume of leachant (m^3)	0.0001		
Leaching renewal flow rate (m^3/s)	0		
Element in M2	**C_0 (mol/L $_{pore}$)**	**S_0 (mol/L $_{pore}$)**	**D (m^2/s)**
Na +K	0.45	0	3 E-11
Ca	0.924	78.8	6 E-11
Cd	3.23 E-04	3.93 E-04	1 E-11
Cr	5.82 E-05	5.99 E-03	4 E-11
Ni	3.93 E-06	1.08 E-03	2 E-10
Solubility (from ANC test)	**M2**		
Cd	log (Ceq) = $-0.0202\,pH^2+0.2649\,pH-6.1227$		
Cr	log (Ceq) = $-0.0057pH^3+0.1016pH^2-0.5348\,pH-2.8412$		
Ni	log (Ceq) = $0.1533pH^2-3.0748pH+8.7895$		

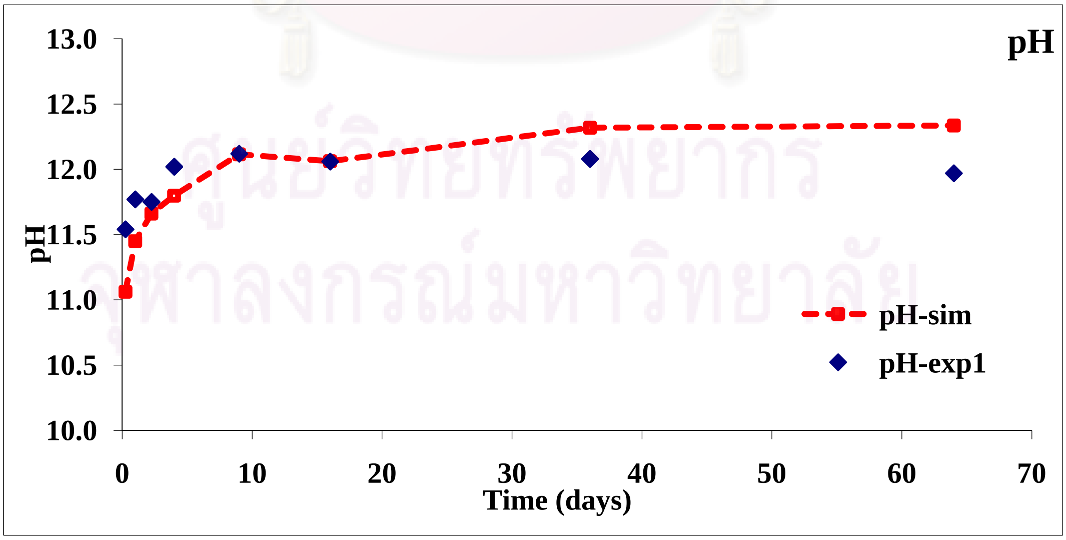


Figure 4.38 Experimental (symbols) and simulated pH for M2 sample (n=5)

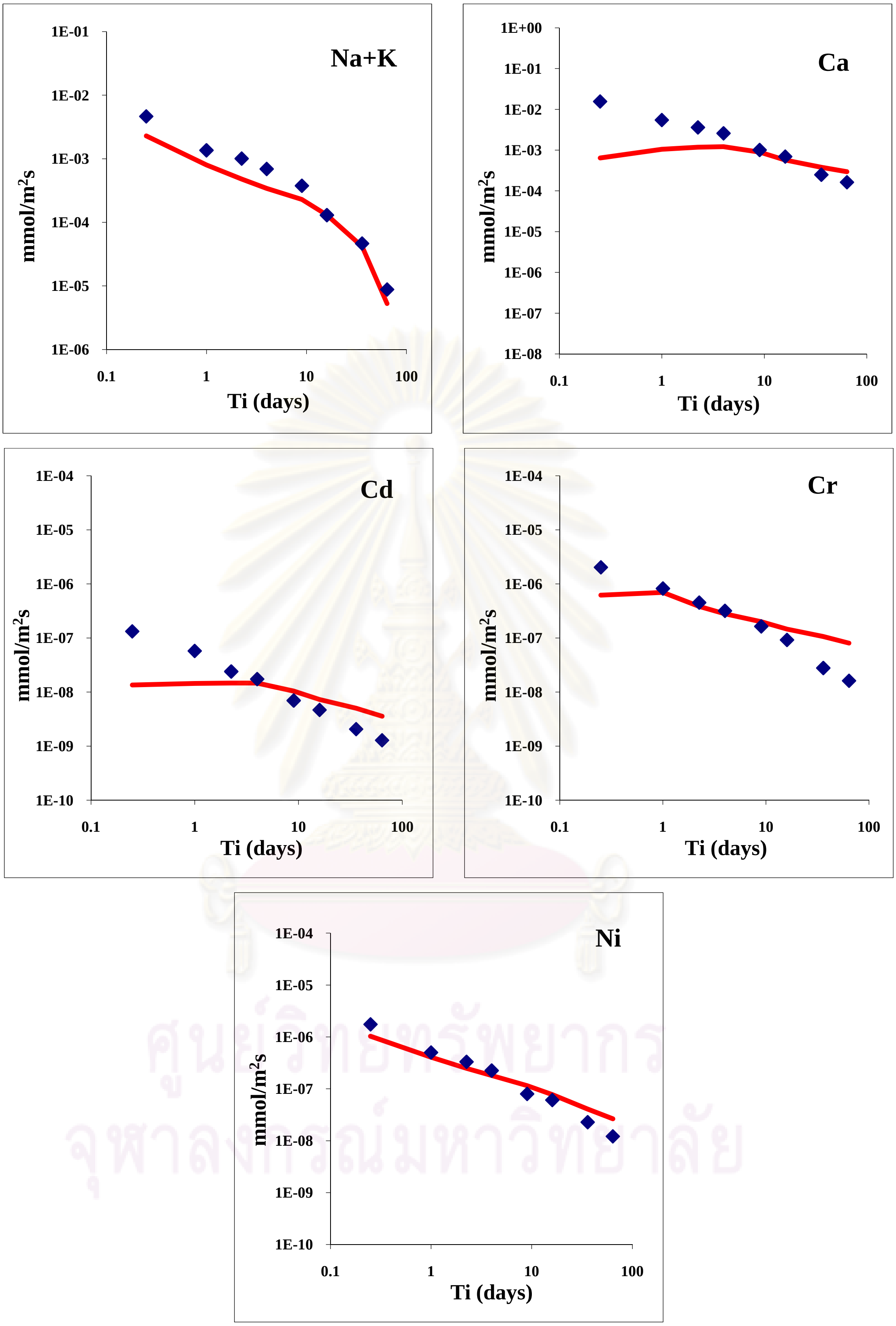


Figure 4.39 Leaching behaviors of Cd, Cr, and Ni (n=5)

CHAPTER V

CONCLUSIONS AND SUGESSTIONS

5.1 Conclusions

The disposal of grinding sludge from iron forging industry must be considered as a serious problem. The well-known and commonly used method for waste disposal such as open dumping and landfilling present many disadvantages. According to the state-of-the-art technique, almost all quantities of spent grinding sludge can be incorporated into cement product. The utilization of grinding sludge in cement manufacture was a successful application as alternative raw materials for partial substitution of the conventional raw materials.

The conclusions derived from the present research work are as follows:

1. The grinding sludge was classified as hazardous waste because the heavy metal content including cadmium, chromium, nickel, and mercury were more than the Thai regulations (DIW, 2005).
2. The grinding sludge could be used as alternative raw material because it had high amount of iron oxide and high heating value.
3. The utilization of grinding sludge in cement production could improve the burnability and reduced the free lime content.
4. The optimal burning condition was 1400°C and 60 minutes.
5. The high substitution of grinding sludge produced some effects on clinker properties. It promoted the formation of C_4AF and slightly supported the formation of C_3S. In contrast, it reduced the formation of C_2S and C_3A.
6. The XRD results of synthesized PC clinker were similar to those of PC clinker from a local cement company.
7. The substitution of grinding sludge was limited at 2% by dry weight.
8. The grinding sludge increased the color of C_3S and size of C_2S.
9. The synthesis the PC clinker in static high temperature furnace found the secondary belite in cement product.

10. The C_4AF preferred to bind with C_3S and the foreign elements tended to incorporate into C_2S.
11. The incorporation of heavy metals including chromium, copper, and nickel were more than 90%.
12. The utilization of grinding sludge as alternative raw materials did not produce impact on the cement properties, especially compressive strength.
13. The results of WET and TCLP of clinker and mortar were below the limits for heavy metal concentrations.
14. About 80-95% of the total Cd, Cr, Mn, and Ni in synthesized PC clinker, cement paste and mortar were associated with the residual fraction. The heavy metals in this fraction were tightly bound with silica oxide and not likely to be released into environment because the silica compounds form the strongest bond in cement.
15. The release of salts in cement mortar was controlled by diffusion mechanism in long-term leaching.
16. The releases of Ca, Cd, and Cr were controlled by surface wash-off and diffusion mechanism.
17. The highest potential release of heavy metal was Ni. The lowest potential release of heavy metals was Cd. The potential risk of constituent in M2 followed Ni > Ca > Cr > Na+K > Cd.

5.2 Recommendations

It is recommended that further research will be undertaken in the following areas:

1. The other cement properties including setting time, grindability, consistency of standard paste, soundness should be further studied.
2. The test burning of waste in demonstration rotary kiln should be investigated.
3. A number of possible future studies using the same experimental set up are apparent in other alternative raw materials and fuel (AFR) before they will use in rotary kiln.
4. The development of new sequential extraction procedure for cement product should be further studied.
5. The setting of environmental criteria in cement should be further developed.

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APPENDICES

APPENDIX A

Chemical composition of clinker

Table A-1 Chemical composition of clinker at 1100 ºC 60 minutes

Chemical Compound	1100 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	19.58	19.45	18.54	18.74	18-22%
Al_2O_3,%	4.47	4.31	4.15	4.04	4-6%
Fe_2O_3 ,%	3.65	5.00	5.94	7.25	2-4%
CaO,%	65.47	64.95	64.04	63.86	60-70%
MgO,%	1.88	1.89	1.86	1.91	The entire content of minor components is commonly under 5%
K_2O,%	0.53	0.47	0.46	0.47	
Na_2O,%	0.11	0.11	0.11	0.11	
SO_3,%	0.17	0.08	0.06	0.07	
P_2O_5,%	0.09	0.09	0.09	0.09	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.22	0.23	0.23	0.23	
Mn_2O_3,%	0.07	0.09	0.11	0.13	
Sum,%	96.24	96.66	95.59	96.92	≈100%
Modulus Equations					
LSF,%	104.81	103.46	105.54	103.07	90-101%
SR,%	2.41	2.09	1.84	1.66	1.4-4.2%
AR,%	1.23	0.86	0.70	0.56	0.6-4.2%
Bogue Equations					
C_3S,%	82.47	80.55	83.41	80.04	55-65%
C_2S,%	-6.08	-5.02	-9.76	-6.64	15-25%
C_3A,%	5.68	2.95	0.95	-1.58	8-14%
C_4AF,%	11.09	15.20	18.05	22.05	8-12%

Table A-2 Chemical composition of clinker at 1200 ºC 60 minutes

Chemical Compound	1200 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	21.68	21.28	21.37	20.60	18-22%
Al_2O_3,%	4.63	4.35	3.98	4.09	4-6%
Fe_2O_3 ,%	3.53	4.98	5.79	6.70	2-4%
CaO,%	66.45	65.57	65.03	64.54	60-70%
MgO,%	1.90	1.85	1.77	1.86	The entire content of minor components is commonly under 5%
K_2O,%	0.45	0.41	0.40	0.39	
Na_2O,%	0.12	0.12	0.12	0.12	
SO_3,%	0.13	0.04	0.04	0.05	
P_2O_5,%	0.09	0.09	0.09	0.09	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.22	0.22	0.21	0.22	
Mn_2O_3,%	0.06	0.09	0.11	0.13	
Sum,%	99.26	99.01	98.92	98.78	≈100%
Modulus Equations					
LSF,%	97.07	96.49	95.22	96.54	90-101%
SR,%	2.66	2.28	2.19	1.91	1.4-4.2%
AR,%	1.31	0.87	0.69	0.61	0.6-4.2%
Bogue Equations					
C_3S,%	69.63	68.86	67.31	69.15	55-65%
C_2S,%	9.63	9.07	10.50	6.89	15-25%
C_3A,%	6.28	3.09	0.75	-0.51	8-14%
C_4AF,%	10.74	15.15	17.60	20.37	8-12%

Table A-3 Chemical composition of clinker at 1300 ºC 60 minutes

Chemical Compound	1300 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	22.62	21.73	20.95	20.60	18-22%
Al_2O_3,%	F13	4.79	4.46	4.38	4-6%
Fe_2O_3 ,%	3.47	4.90	6.52	8.55	2-4%
CaO,%	65.44	64.50	63.86	62.04	60-70%
MgO,%	1.98	2.00	2.00	2.03	The entire content of minor components is commonly under 5%
K_2O,%	0.27	0.25	0.26	0.30	
Na_2O,%	0.13	0.12	0.12	0.12	
SO_3,%	0.08	0.04	0.05	0.06	
P_2O_5,%	0.09	0.09	0.09	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.24	0.24	0.24	0.25	
Mn_2O_3,%	0.07	0.10	0.13	0.18	
Sum,%	99.61	98.75	98.69	98.59	≈100%
Modulus Equations					
LSF,%	91.21	92.58	93.68	90.69	90-101%
SR,%	2.60	2.24	1.91	1.59	1.4-4.2%
AR,%	1.50	0.98	0.68	0.51	0.6-4.2%
Bogue Equations					
C_3S,%	54.48	58.30	61.46	54.35	55-65%
C_2S,%	23.74	18.32	13.71	20.19	15-25%
C_3A,%	7.96	4.39	0.78	-2.86	8-14%
C_4AF,%	10.55	14.89	19.82	25.99	8-12%

Table A-4 Chemical composition of clinker at 1350 ºC 60 minutes

Chemical Compound	1350 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	23.59	21.93	20.93	20.07	18-22%
Al_2O_3,%	5.45	4.98	4.60	4.41	4-6%
Fe_2O_3 ,%	3.25	4.96	6.53	8.61	2-4%
CaO,%	64.71	64.58	63.75	62.08	60-70%
MgO,%	1.99	1.95	1.94	1.94	The entire content of minor components is commonly under 5%
K_2O,%	0.32	0.29	0.32	0.35	
Na_2O,%	0.13	0.13	0.13	0.12	
SO_3,%	0.07	0.06	0.05	0.07	
P_2O_5,%	0.09	0.09	0.08	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.25	0.24	0.25	0.25	
Mn_2O_3,%	0.07	0.10	0.13	0.18	
Sum,%	99.92	99.31	98.70	98.18	≈100%
Modulus Equations					
LSF,%	88.74	91.61	93.37	92.66	90-101%
SR,%	2.71	2.21	1.88	1.54	1.4-4.2%
AR,%	1.68	1.01	0.70	0.51	0.6-4.2%
Bogue Equations					
C_3S,%	42.86	55.69	60.20	58.24	55-65%
C_2S,%	35.30	20.85	14.58	13.61	15-25%
C_3A,%	8.95	4.82	1.14	-2.87	8-14%
C_4AF,%	9.88	15.06	19.86	26.16	8-12%

Table A-5 Chemical composition of clinker at 1400 ºC 60 minutes

Chemical Compound	1400 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	22.31	21.82	21.15	20.12	18-22%
Al_2O_3,%	5.12	5.15	4.92	4.43	4-6%
Fe_2O_3 ,%	3.53	5.09	6.71	8.50	2-4%
CaO,%	65.49	64.49	63.44	62.29	60-70%
MgO,%	1.89	1.89	1.86	1.95	The entire content of minor components is commonly under 5%
K_2O,%	0.18	0.25	0.35	0.31	
Na_2O,%	0.12	0.12	0.12	0.12	
SO_3,%	0.08	0.04	0.04	0.05	
P_2O_5,%	0.09	0.09	0.09	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.24	0.24	0.24	0.25	
Mn_2O_3,%	0.07	0.10	0.13	0.17	
Sum,%	99.12	99.28	99.05	98.29	≈100%
Modulus Equations					
LSF,%	92.48	91.50	91.45	92.87	90-101%
SR,%	2.58	2.13	1.82	1.56	1.4-4.2%
AR,%	1.45	1.01	0.73	0.52	0.6-4.2%
Bogue Equations					
C_3S,%	57.57	54.85	54.93	58.79	55-65%
C_2S,%	20.54	21.18	19.18	13.32	15-25%
C_3A,%	7.60	5.04	1.68	-2.65	8-14%
C_4AF,%	10.74	15.46	20.40	25.85	8-12%

TableA-6 Chemical composition of clinker at 1450 ºC at 60 minutes

Chemical Compound	1450 ºC at 60 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	23.81	21.85	21.11	19.85	18-22%
Al_2O_3,%	6.37	5.63	4.96	5.24	4-6%
Fe_2O_3 ,%	3.36	5.11	6.61	9.39	2-4%
CaO,%	64.16	64.25	63.49	61.33	60-70%
MgO,%	1.75	1.83	1.89	1.93	The entire content of minor components is commonly under 5%
K_2O,%	0.26	0.26	0.32	0.37	
Na_2O,%	0.13	0.12	0.12	0.12	
SO_3,%	0.09	0.05	0.04	0.05	
P_2O_5,%	0.09	0.08	0.08	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.25	0.25	0.24	0.26	
Mn_2O_3,%	0.07	0.10	0.13	0.19	
Sum,%	100.34	99.55	99.00	98.82	≈100%
Modulus Equations					
LSF,%	84.01	90.31	91.69	90.36	90-101%
SR,%	2.45	2.03	1.83	1.36	1.4-4.2%
AR,%	1.90	1.10	0.75	0.56	0.6-4.2%
Bogue Equations					
C_3S,%	32.62	50.38	55.29	50.19	55-65%
C_2S,%	43.65	24.64	18.80	19.06	15-25%
C_3A,%	11.20	6.26	1.95	-2.00	8-14%
C_4AF,%	10.22	15.54	20.09	28.54	8-12%

Table A-7 Chemical composition of clinker at 1400 ºC at 30 minutes

Chemical Compound	1400 ºC at 30 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	23.40	22.81	21.69	19.85	18-22%
Al_2O_3,%	5.27	5.06	4.75	4.43	4-6%
Fe_2O_3 ,%	4.09	4.97	6.63	8.50	2-4%
CaO,%	64.25	63.84	63.02	62.67	60-70%
MgO,%	1.93	1.95	1.94	1.98	The entire content of minor components is commonly under 5%
K_2O,%	0.27	0.29	0.32	0.31	
Na_2O,%	0.13	0.13	0.12	0.13	
SO_3,%	0.05	0.04	0.04	0.05	
P_2O_5,%	0.09	0.09	0.09	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.25	0.25	0.26	0.25	
Mn_2O_3,%	0.09	0.10	0.14	0.17	
Sum,%	99.82	99.53	98.99	98.43	≈100%
Modulus Equations					
LSF,%	86.36	87.36	89.20	94.50	90-101%
SR,%	2.50	2.27	1.91	1.54	1.4-4.2%
AR,%	1.29	1.02	0.72	0.52	0.6-4.2%
Bogue Equations					
C_3S,%	42.47	45.42	50.33	62.41	55-65%
C_2S,%	35.05	31.14	24.22	9.82	15-25%
C_3A,%	7.05	5.00	1.36	-2.65	8-14%
C_4AF,%	12.42	15.11	20.15	25.83	8-12%

Table A-8 Chemical composition of clinker at 1400 ºC at 75 minutes

Chemical Compound	1400 ºC at 75 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	22.77	22.87	21.61	19.87	18-22%
Al_2O_3,%	5.45	5.11	4.79	4.56	4-6%
Fe_2O_3 ,%	4.15	4.99	6.72	8.45	2-4%
CaO,%	64.01	63.70	62.88	62.63	60-70%
MgO,%	1.92	1.93	1.94	1.97	The entire content of minor components is commonly under 5%
K_2O,%	0.18	0.22	0.29	0.30	
Na_2O,%	0.12	0.12	0.12	0.12	
SO_3,%	0.09	0.05	0.04	0.05	
P_2O_5,%	0.09	0.09	0.09	0.08	
Cl,%	0.01	0.00	0.01	0.01	
TiO_2,%	0.25	0.25	0.25	0.26	
Mn_2O_3,%	0.09	0.10	0.14	0.17	
Sum,%	99.11	99.43	98.88	98.47	≈100%
Modulus Equations					
LSF,%	87.81	86.90	89.15	94.16	90-101%
SR,%	2.37	2.26	1.88	1.53	1.4-4.2%
AR,%	1.31	1.03	0.71	0.54	0.6-4.2%
Bogue Equations					
C_3S,%	44.95	44.05	49.97	61.21	55-65%
C_2S,%	31.39	32.33	24.27	10.80	15-25%
C_3A,%	7.42	5.11	1.31	-2.21	8-14%
C_4AF,%	12.61	15.16	20.44	25.69	8-12%

Table A-9 Chemical composition of clinker at 1450 ºC at 30 minutes

Chemical Compound	1450 ºC at 30 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	23.86	22.52	21.44	20.71	18-22%
Al_2O_3,%	5.65	5.18	4.70	4.51	4-6%
Fe_2O_3 ,%	3.35	5.00	6.72	8.62	2-4%
CaO,%	64.39	63.88	63.07	61.98	60-70%
MgO,%	1.90	1.89	1.94	1.97	The entire content of minor components is commonly under 5%
K_2O,%	0.22	0.24	0.32	0.35	
Na_2O,%	0.20	0.12	0.12	0.12	
SO_3,%	0.06	0.04	0.04	0.05	
P_2O_5,%	0.09	0.09	0.08	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.25	0.25	0.25	0.25	
Mn_2O_3,%	0.07	0.10	0.14	0.18	
Sum,%	100.04	99.31	98.82	98.82	≈100%
Modulus Equations					
LSF,%	85.12	88.23	90.17	89.97	90-101%
SR,%	2.65	2.21	1.88	1.58	1.4-4.2%
AR,%	1.69	1.04	0.70	0.52	0.6-4.2%
Bogue Equations					
C_3S,%	38.07	47.02	52.60	52.36	55-65%
C_2S,%	39.68	29.08	21.78	19.86	15-25%
C_3A,%	9.30	5.27	1.10	-2.62	8-14%
C_4AF,%	10.19	15.19	20.43	26.19	8-12%

Table A-10 Chemical composition of clinker at 1450 ºC at 75 minutes

Chemical Compound	1450 ºC at 75 minutes				
	M0	M1	M2	M3	Range
SiO_2,%	23.84	22.54	21.56	20.15	18-22%
Al_2O_3,%	5.68	5.34	4.77	4.94	4-6%
Fe_2O_3 ,%	3.33	5.03	6.64	8.91	2-4%
CaO,%	64.28	63.89	63.17	61.69	60-70%
MgO,%	1.86	1.86	1.91	1.97	The entire content of minor components is commonly under 5%
K_2O,%	0.16	0.26	0.30	0.32	
Na_2O,%	0.12	0.12	0.12	0.12	
SO_3,%	0.07	0.04	0.04	0.05	
P_2O_5,%	0.09	0.09	0.09	0.08	
Cl,%	0.01	0.01	0.01	0.01	
TiO_2,%	0.25	0.25	0.24	0.25	
Mn_2O_3,%	0.07	0.10	0.14	0.18	
Sum,%	99.74	Q64	98.98	98.66	≈100%
Modulus Equations					
LSF,%	85.01	87.91	89.86	90.68	90-101%
SR,%	2.65	2.17	1.89	1.45	1.4-4.2%
AR,%	1.71	1.06	0.72	0.55	0.6-4.2%
Bogue Equations					
C_3S,%	37.60	45.75	51.80	52.09	55-65%
C_2S,%	39.99	30.10	22.72	18.46	15-25%
C_3A,%	9.41	5.65	1.42	-1.99	8-14%
C_4AF,%	10.11	15.28	20.17	27.09	8-12%

APPENDIX B

The mineralogical results of synthesized PC clinker

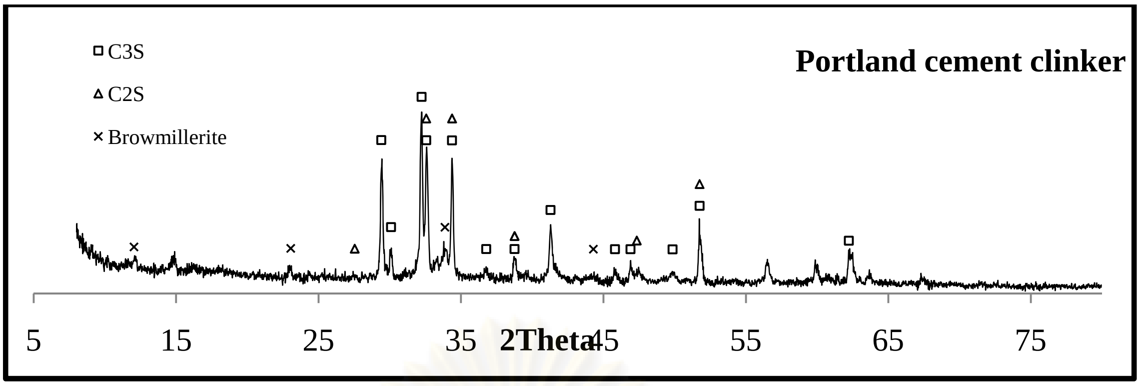


Figure B-1 XRD of Portland cement clinker without grinding sludge

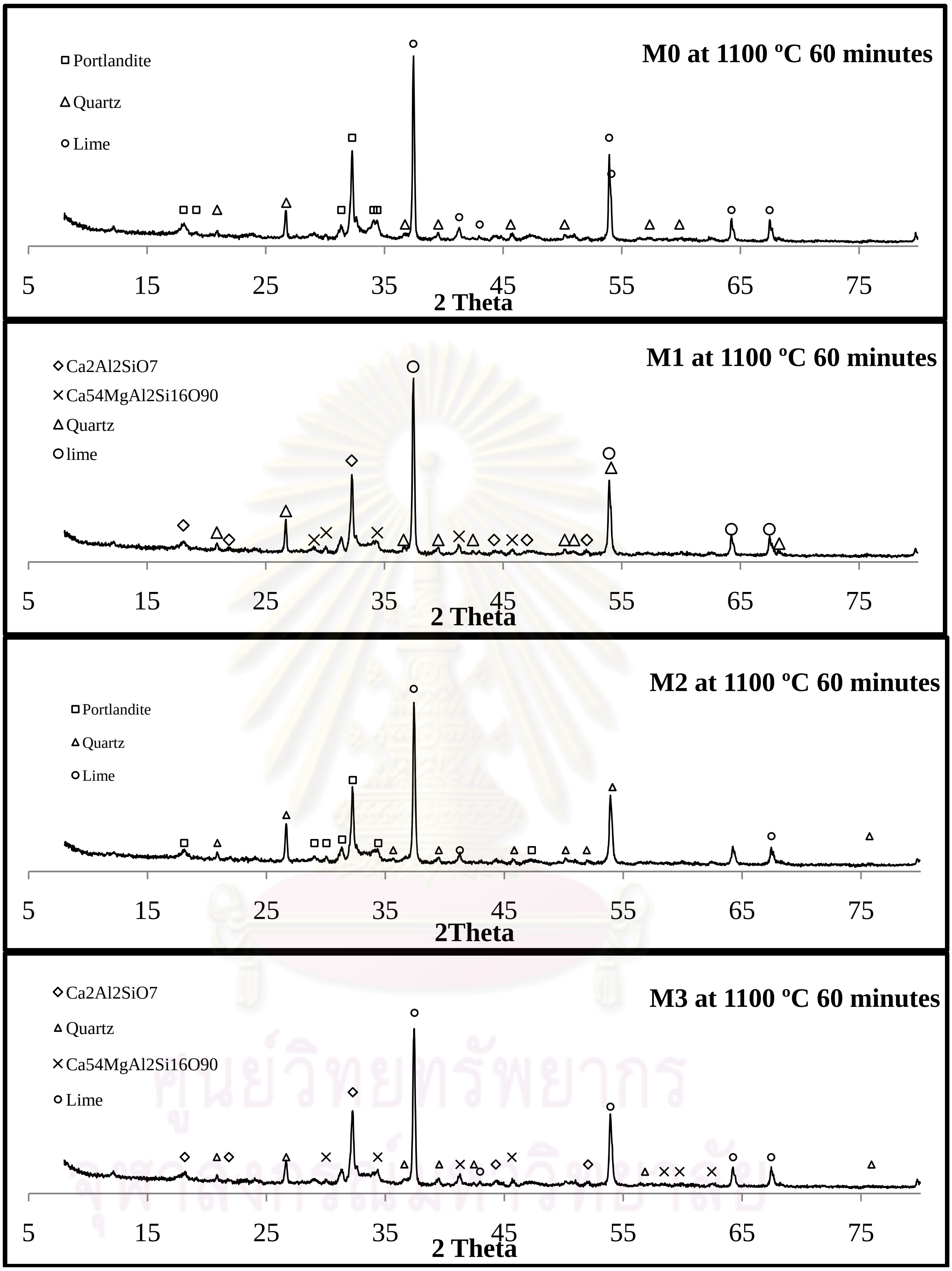


Figure B-2 XRD of Portland cement clinker with grinding sludge at 1100°C 1 hour

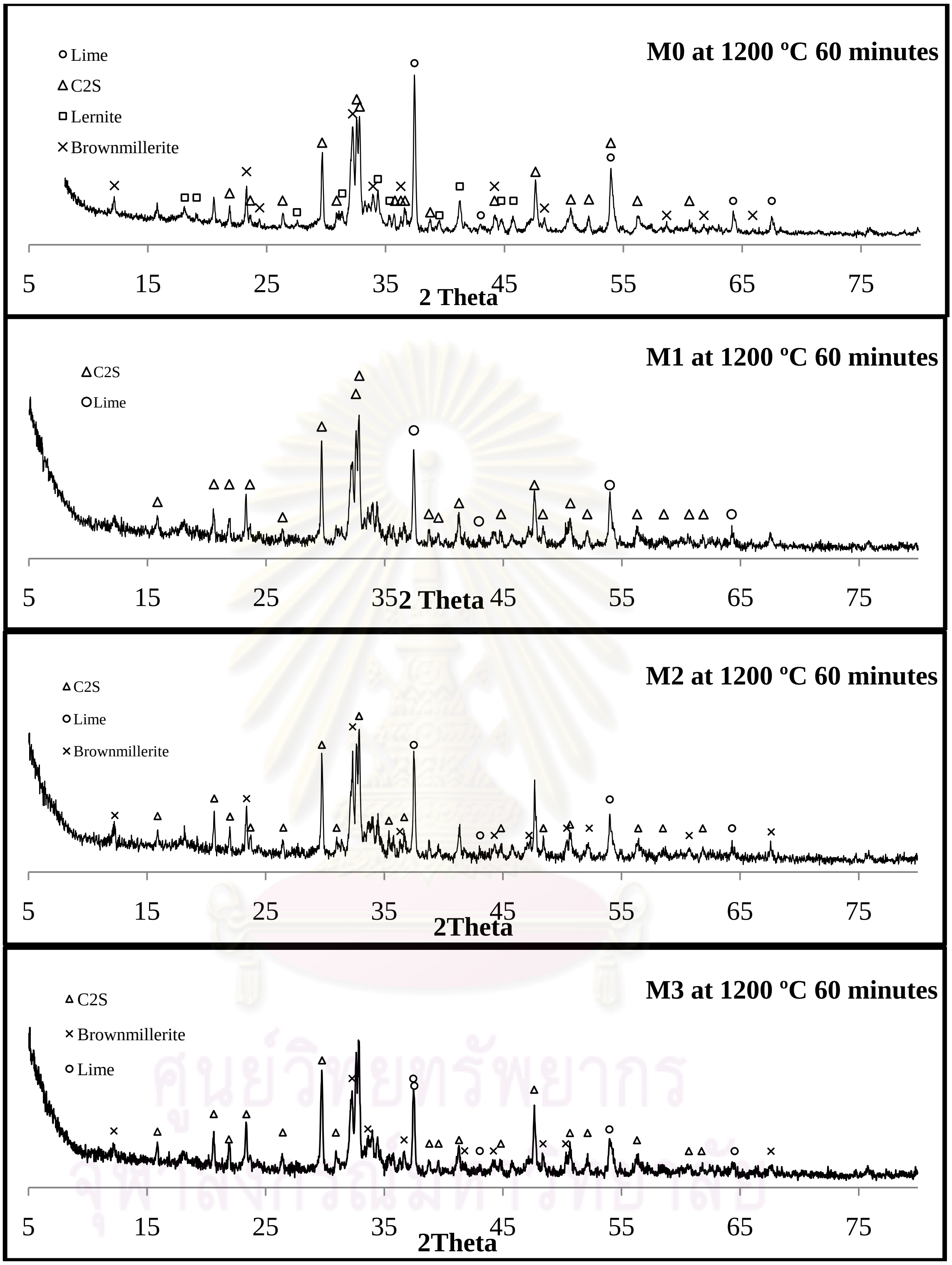


Figure B-3 XRD of Portland cement clinker with grinding sludge at 1200°C 1 hour

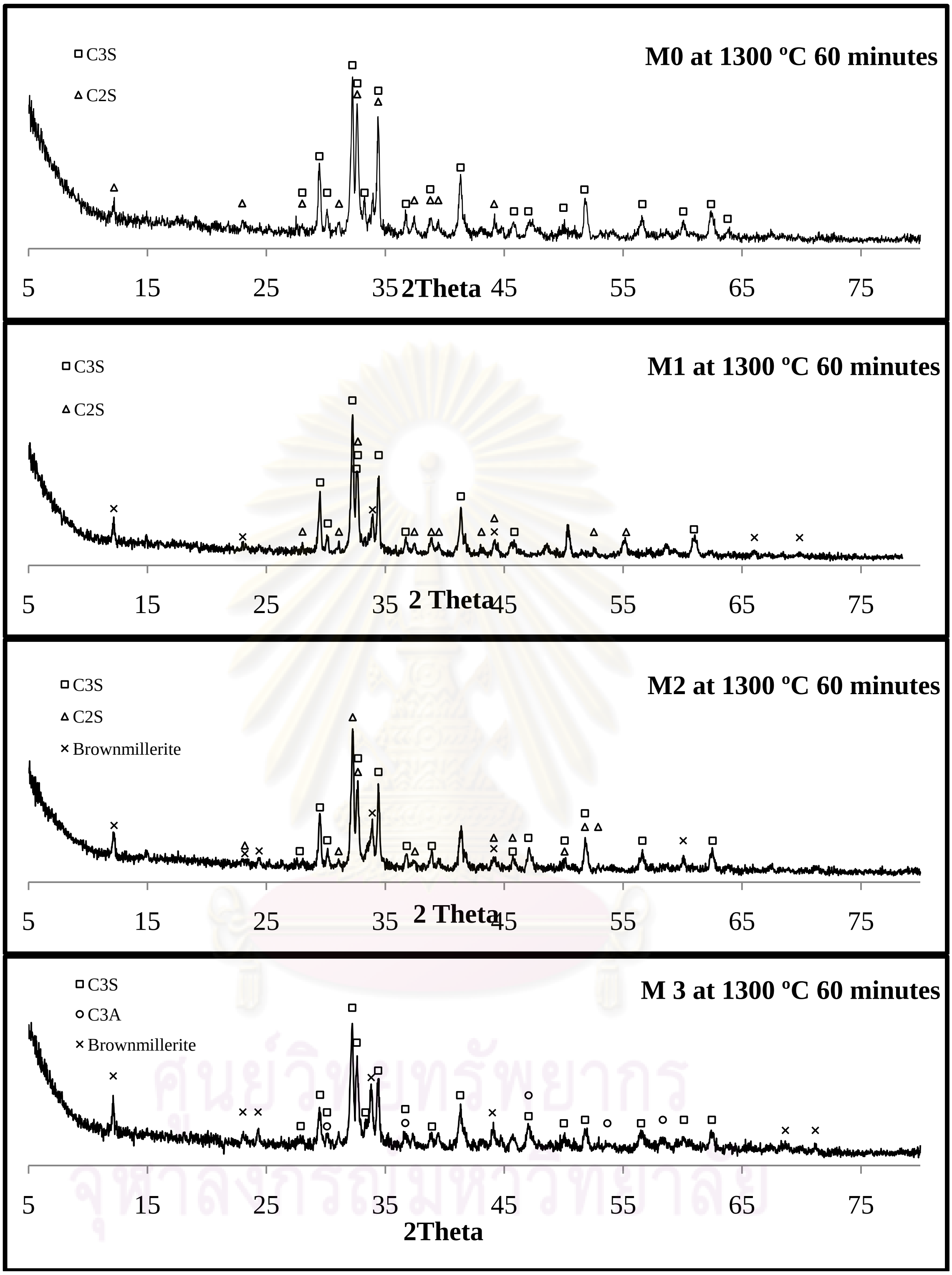


Figure B-4 XRD of Portland cement clinker with grinding sludge at 1300°C 1 hour

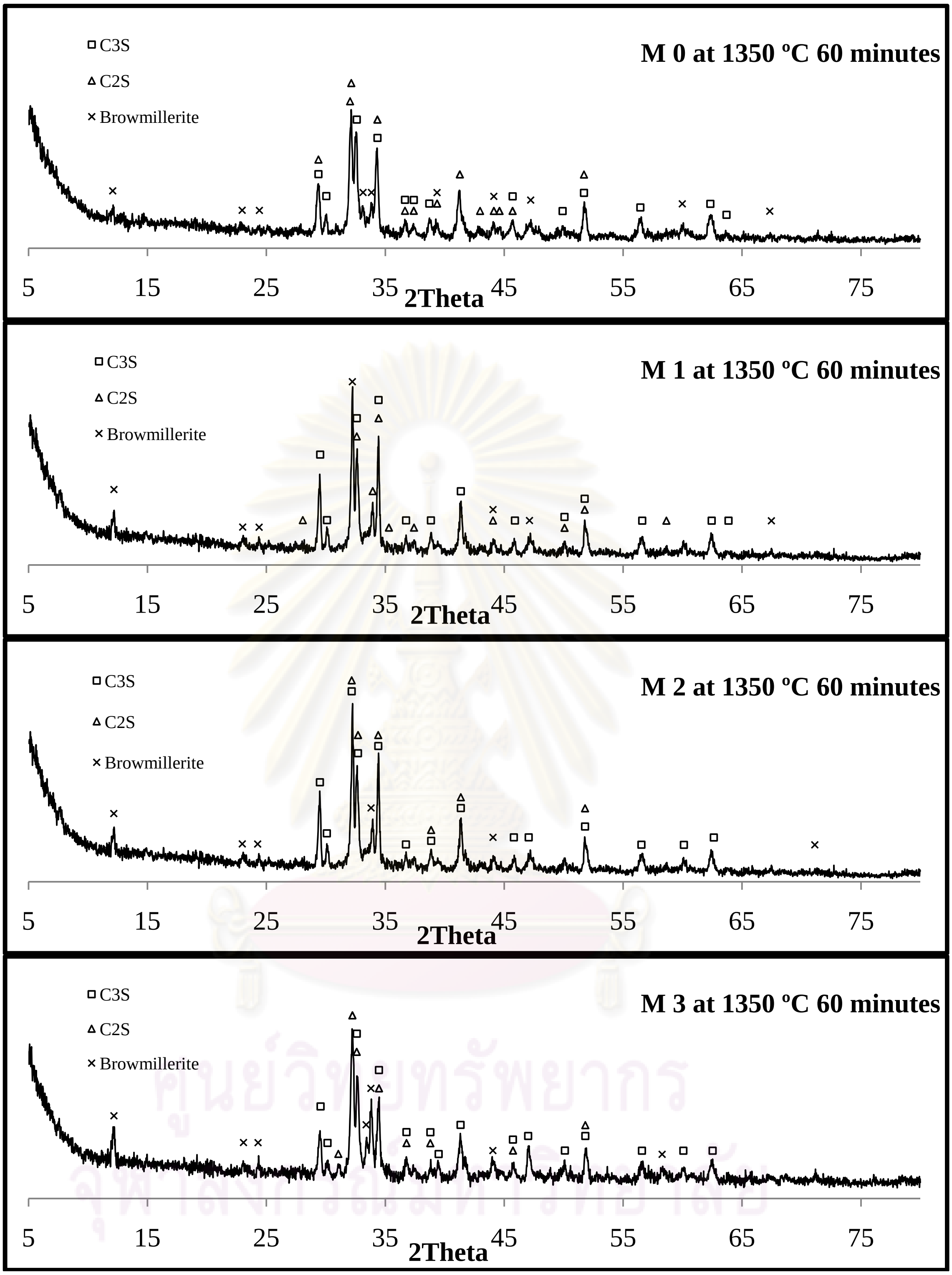


Figure B-5 XRD of Portland cement clinker with grinding sludge at 1350°C 1 hour

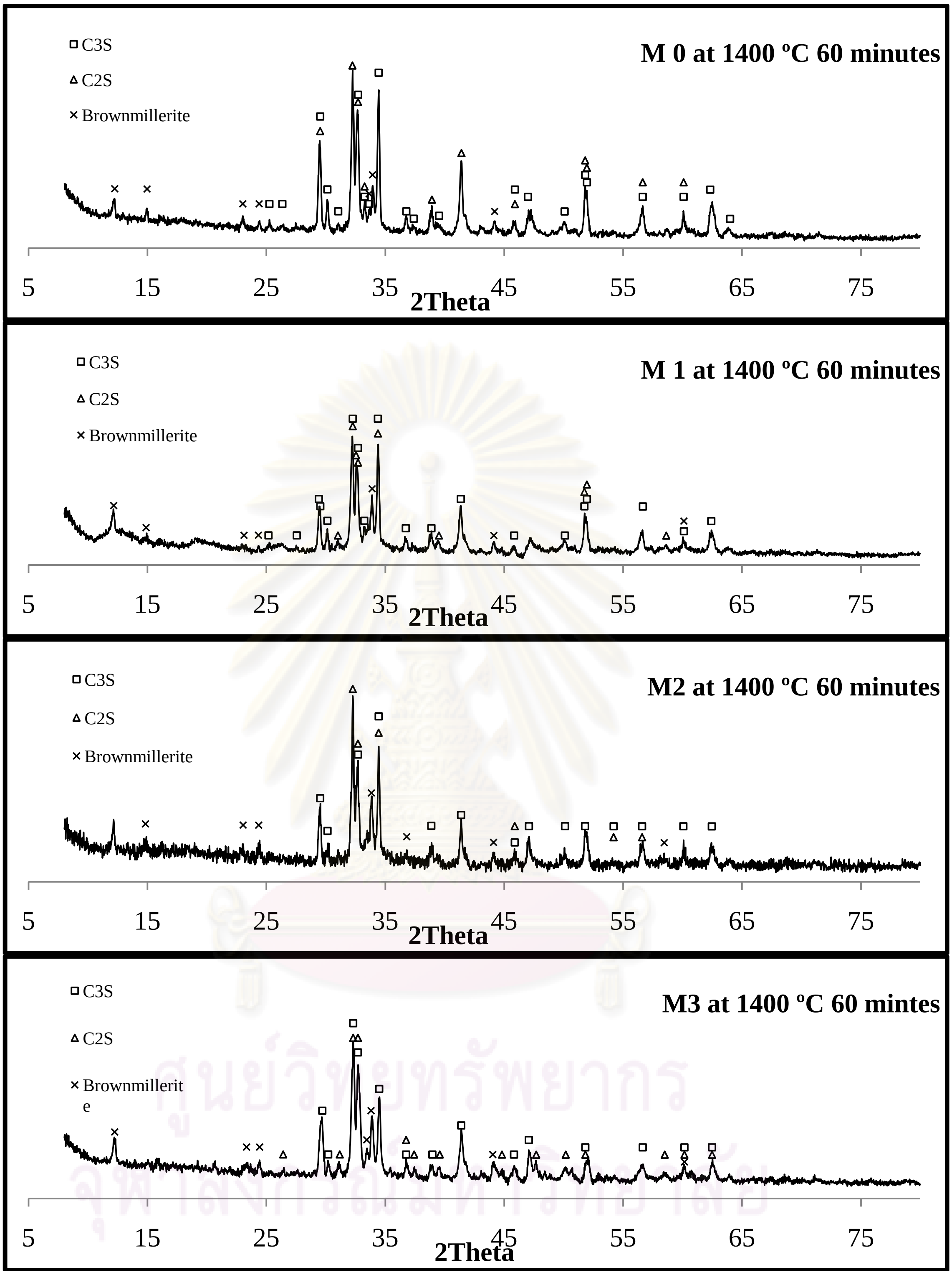


Figure B-6 XRD of Portland cement clinker with grinding sludge at 1400°C 1 hour

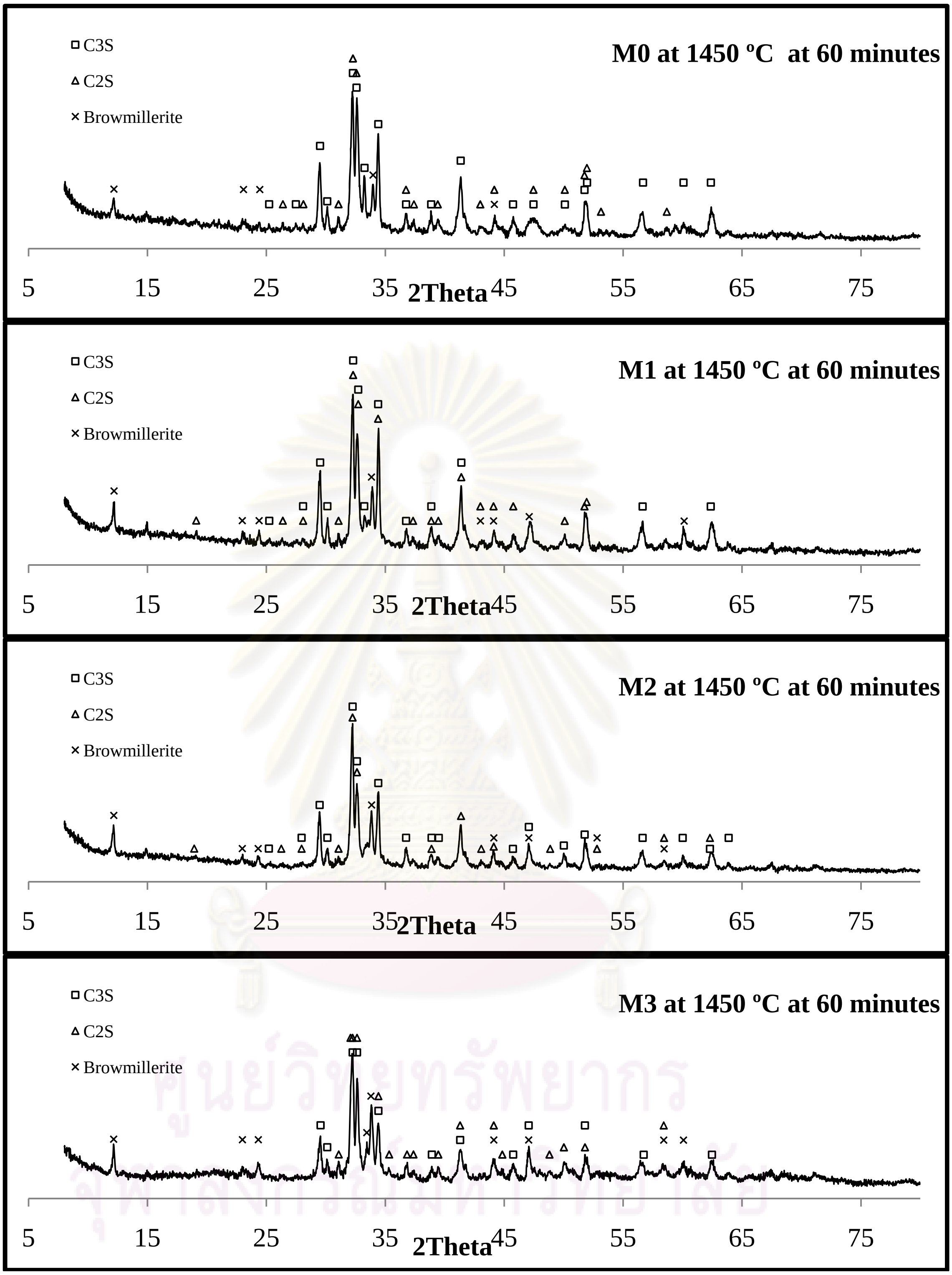


Figure B-7 XRD of Portland cement clinker with grinding sludge at 1450°C 1 hour

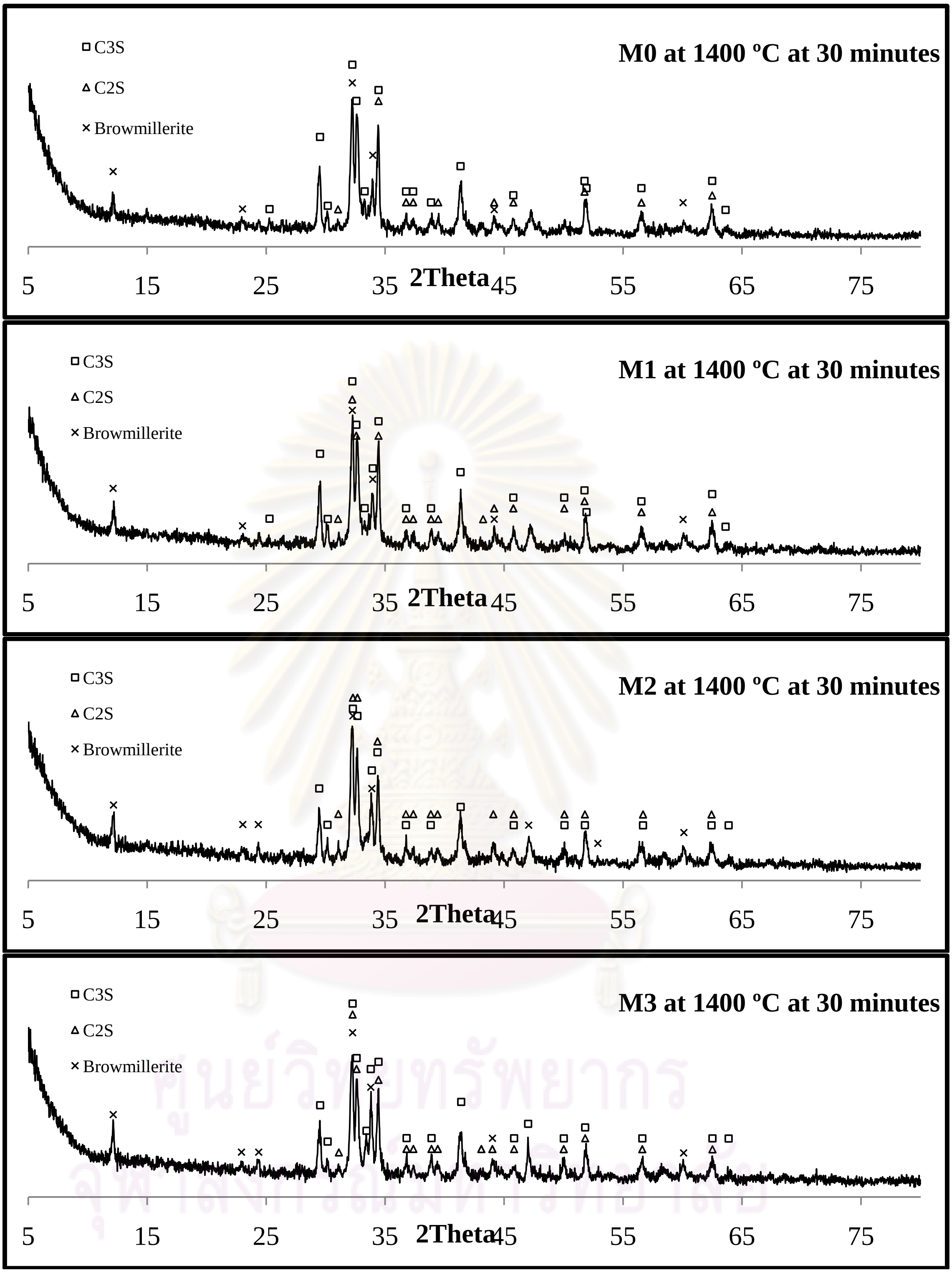


Figure B-8 XRD of Portland cement clinker with grinding sludge at 1400°C 30 minutes

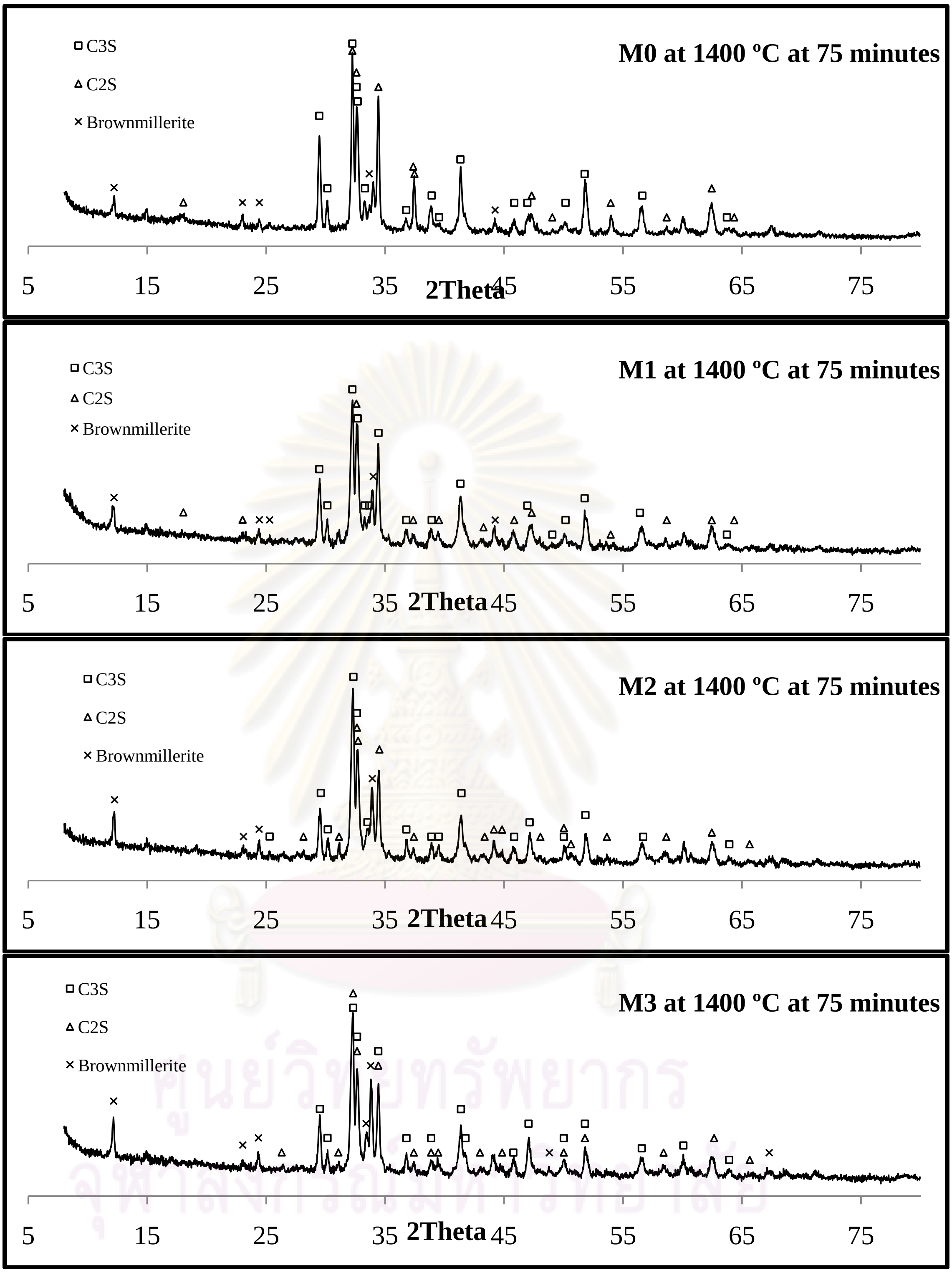


Figure B-9 XRD of Portland cement clinker with grinding sludge at 1400°C 75 minutes

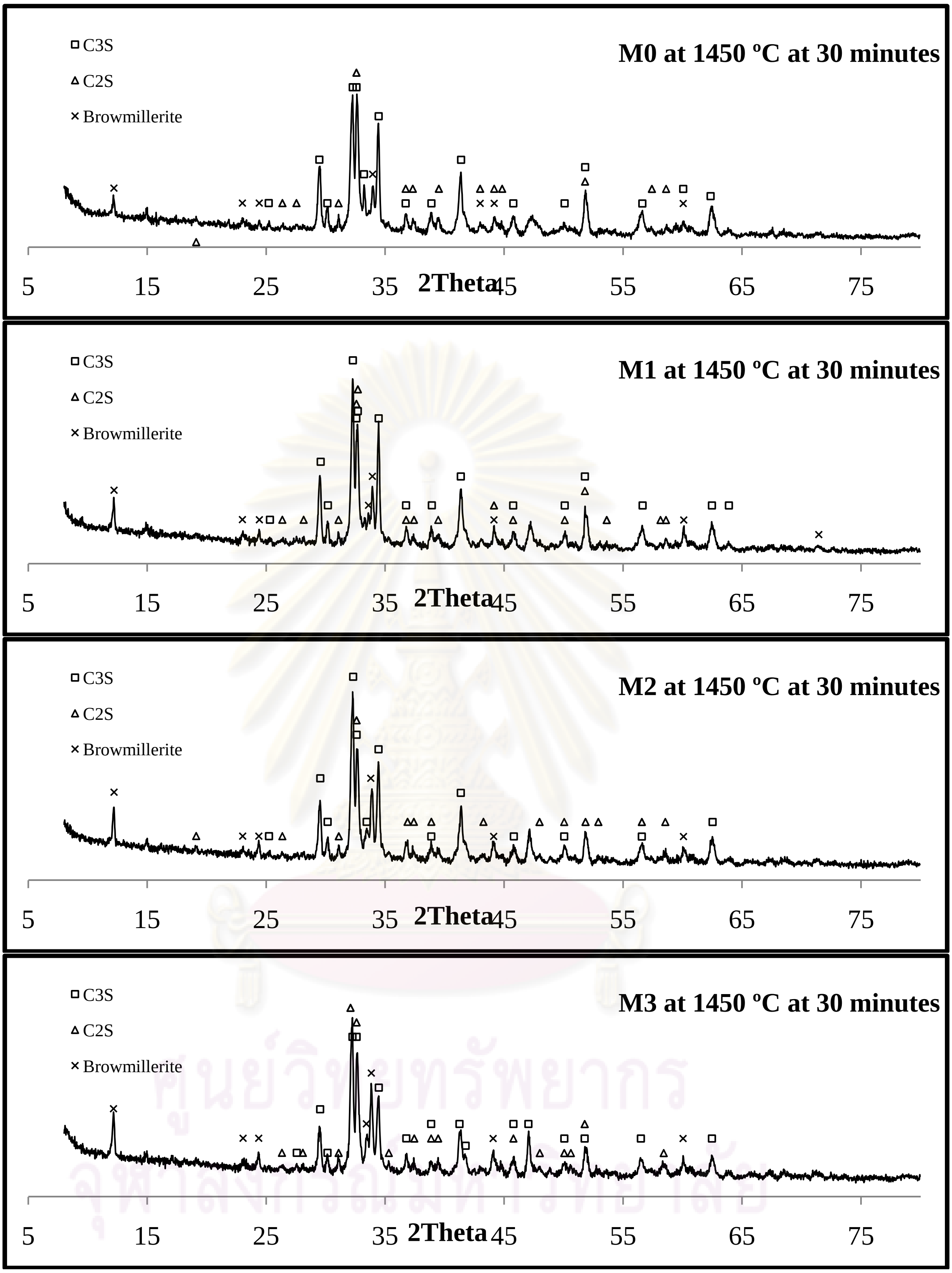


Figure B-10 XRD of Portland cement clinker with grinding sludge at 1450°C 30 minutes

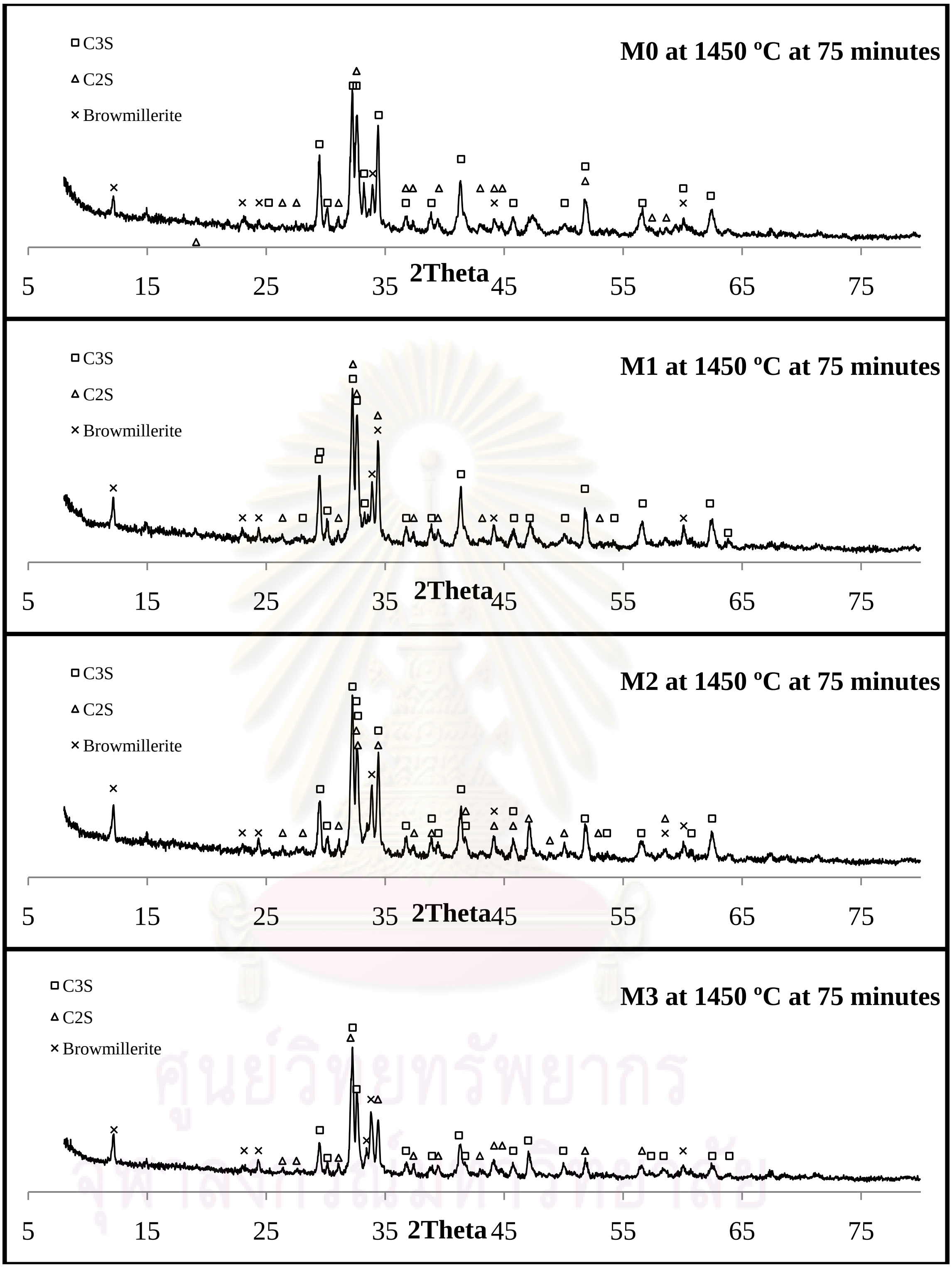
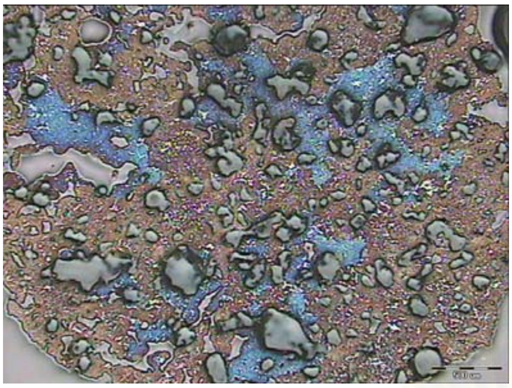


Figure B-11 XRD of Portland cement clinker with grinding sludge at 1450°C 75 minutes

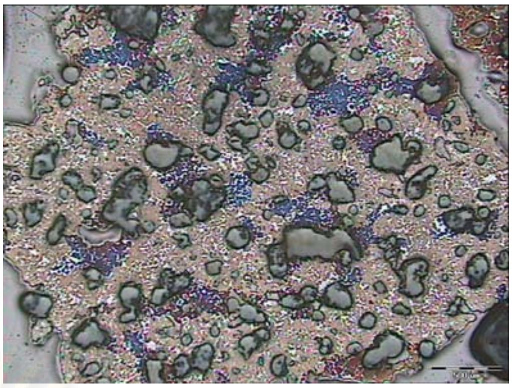
APPENDIX C

Optical Microscopic Results

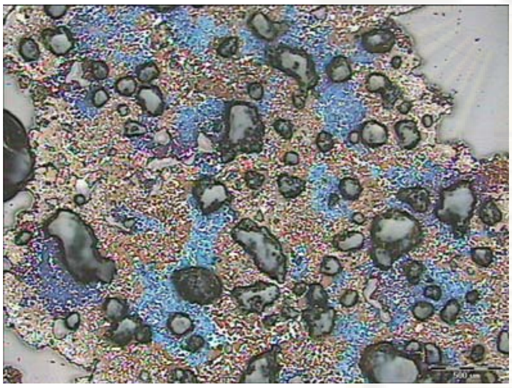
1400_0%_5x



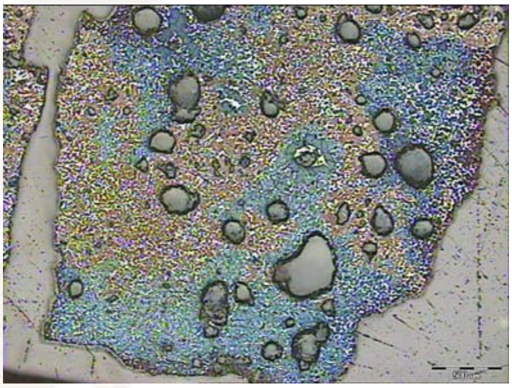
1400_1%_5x



1400_2%_5x



1400_3%_5x



Real_5x

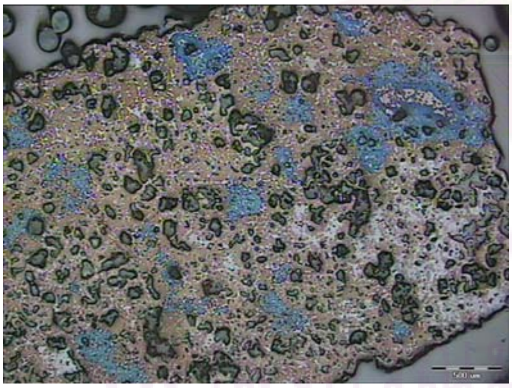
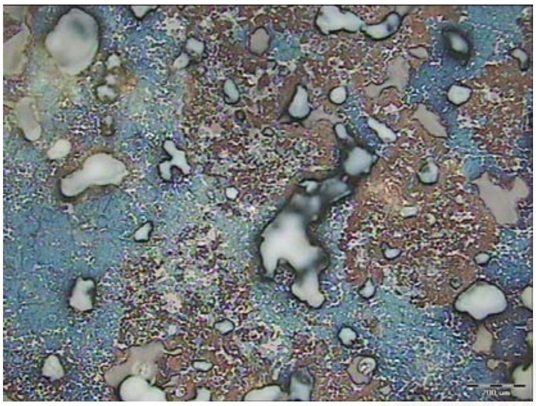
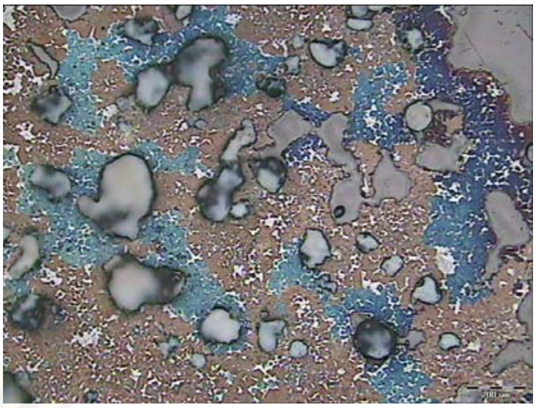


Figure C-1 optical microscope at 5x magnification

1400_0%_10x

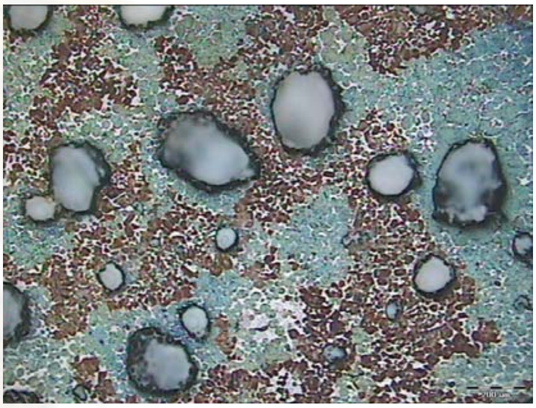


1400_1%_10x



1400_2%_10x

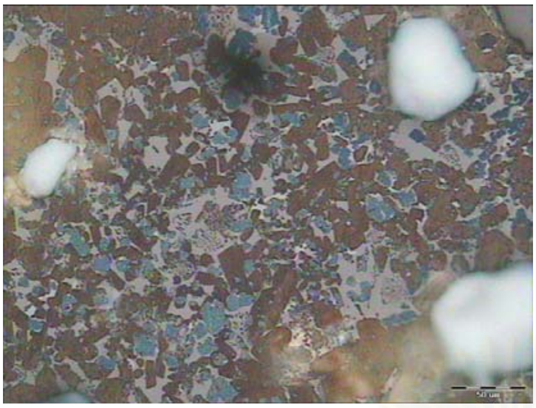
1400_3%_10x



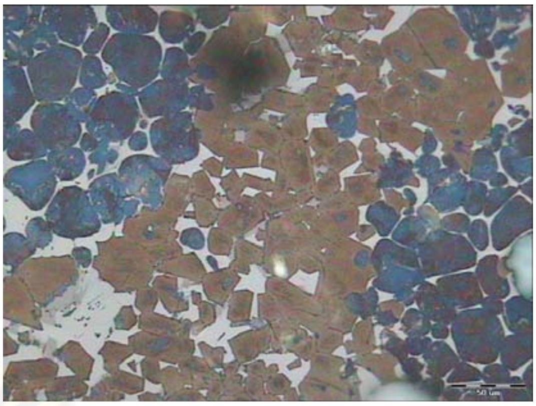
Real_10x

Figure C-2 optical microscope at 10x magnification

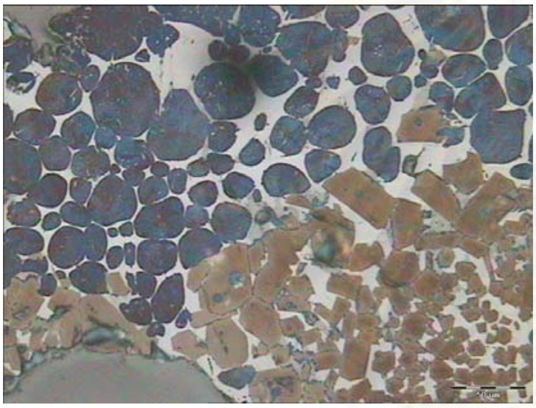
1400_0%_50x



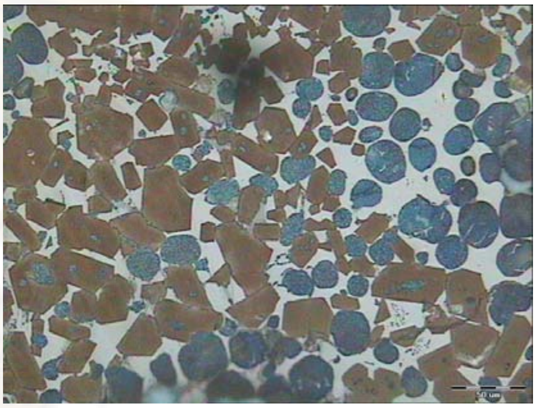
1400_1%_50x



1400_2%_50x



1400_3%_50x



Real_50x

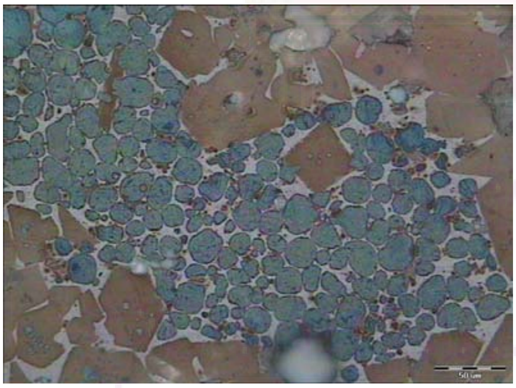
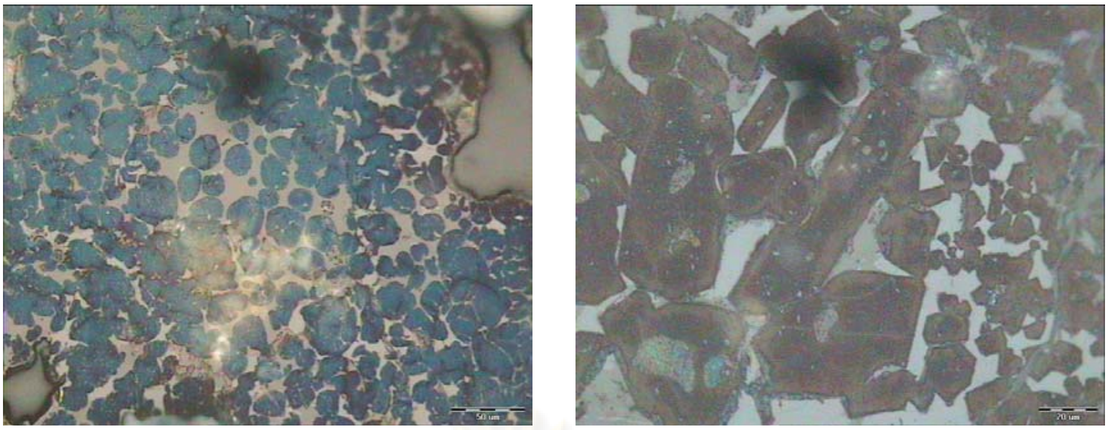
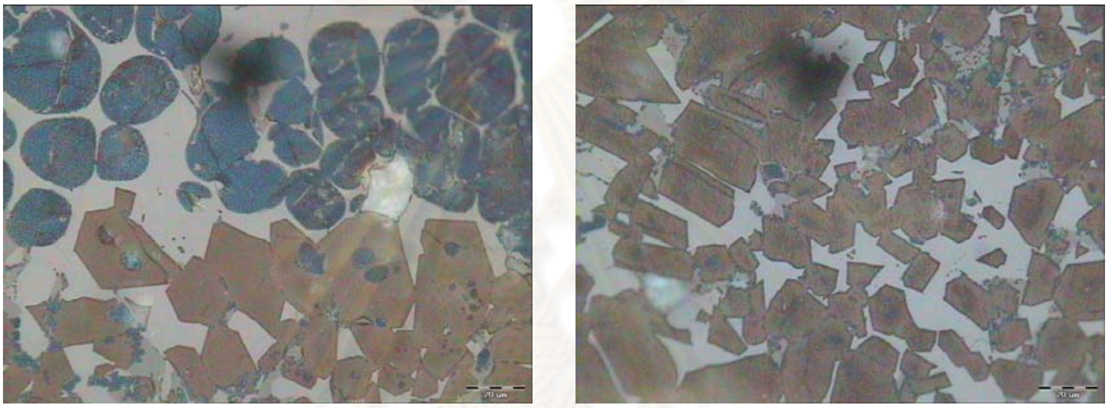


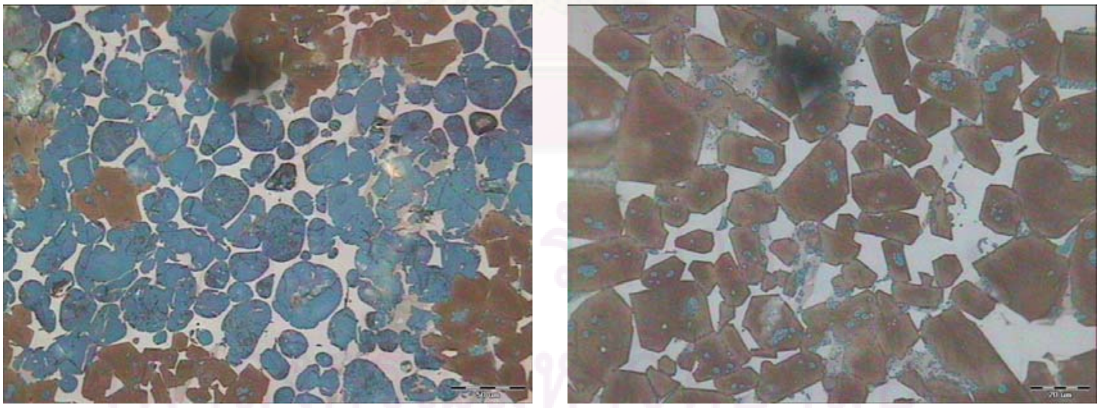
Figure C-3 optical microscope at 50x magnification



1400C_0%_100x

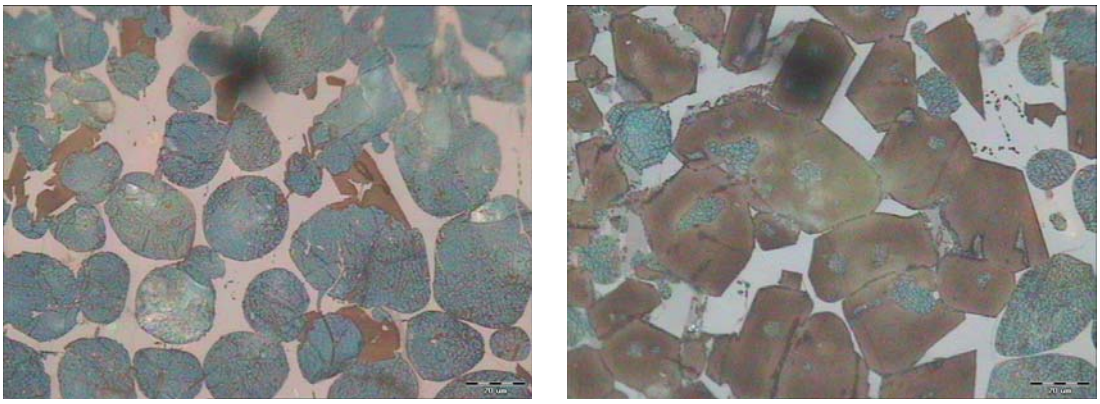


1400C_1%_100x

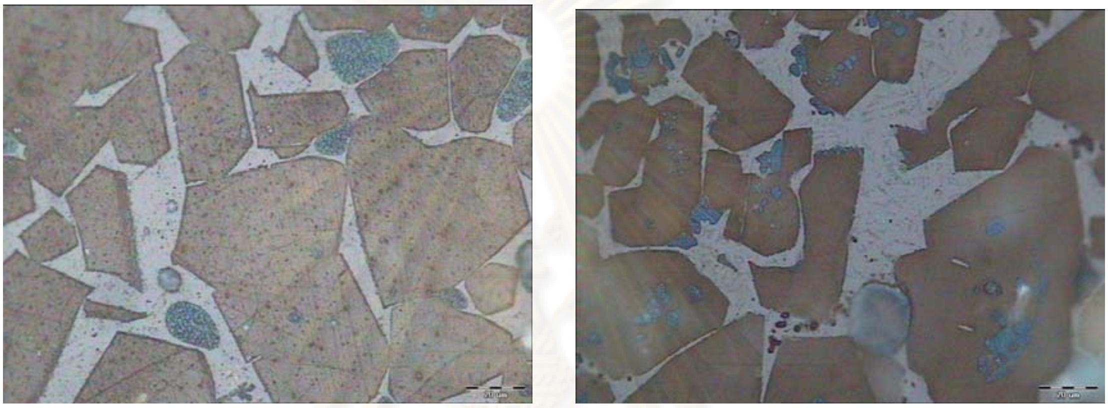


1400C_2%_100x

Figure C-4 optical microscope at 100x magnification



1400C_3%_100x



Real_100x

Figure C-5 optical microscope at 100x magnification

APPENDIX D

Pore water test results

Table D-1 The PW test results of M2 (Alumina, Iron and Sodium)

L/S	Al			
	Mw	26.98154		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0493	0.0018	-1.3068	-2.7378
1	0.0961	0.0036	-1.0173	-2.4483
5	0.2248	0.0083	-0.6482	-2.0792
10	0.7910	0.0293	-0.1018	-1.5329
20	0.2150	0.0080	-0.6675	-2.0985
50	0.3467	0.0128	-0.4600	-1.8911
100	1.6163	0.0599	0.2085	-1.2225
L/S	Fe			
	MW	55.845		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0925	0.0017	-1.0340	-2.7810
1	0.0688	0.0012	-1.1625	-2.9095
5	0.0691	0.0012	-1.1606	-2.9076
10	0.0816	0.0015	-1.0885	-2.8354
20	0.0832	0.0015	-1.0800	-2.8270
50	0.0797	0.0014	-1.0984	-2.8454
100	0.1518	0.0027	-0.8186	-2.5656
L/S	Na			
	MW	22.98977		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	279.9500	12.1772	2.4471	1.0855
1	154.2400	6.7091	2.1882	0.8267
5	34.2460	1.4896	1.5346	0.1731
10	4.4117	0.1919	0.6446	-0.7169
20	16.5070	0.7180	1.2177	-0.1439
50	8.9757	0.3904	0.9531	-0.4085
100	2.6557	0.1155	0.4242	-0.9374

Table D-2 The PW test results of M2 (Calcium, Potassium and Nickel)

L/S	Ca			
	Mw	40.078		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	11.4140	0.2848	1.0574	-0.5455
1	315.4200	7.8702	2.4989	0.8960
5	416.1700	10.3840	2.6193	1.0164
10	207.0400	5.1659	2.3161	0.7131
20	223.9600	5.5881	2.3502	0.7473
50	275.2500	6.8679	2.4397	0.8368
100	141.2000	3.5231	2.1498	0.5469
L/S	K			
	MW	39.0983		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	462.5100	11.8294	2.6651	1.0730
1	276.7500	7.0783	2.4421	0.8499
5	69.7920	1.7850	1.8438	0.2516
10	88.0350	2.2516	1.9447	0.3525
20	34.1530	0.8735	1.5334	-0.0587
50	19.4500	0.4975	1.2889	-0.3032
100	17.6990	0.4527	1.2479	-0.3442
L/S	Ni			
	MW	58.6934		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0710	0.0012	-1.1487	-2.9173
1	0.0980	0.0017	-1.0088	-2.7774
5	0.0870	0.0015	-1.0605	-2.8291
10	0.0950	0.0016	-1.0223	-2.7909
20	0.0780	0.0013	-1.1079	-2.8765
50	0.0770	0.0013	-1.1135	-2.8821
100	0.1180	0.0020	-0.9281	-2.6967

Table D-3 The PW test results of M2 (Cadmium, Lithium, and Lead)

L/S	Cd 214.			
	MW	112.411		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0113	0.0001	-1.9469	-3.9977
1	0.0128	0.0001	-1.8928	-3.9436
5	0.0064	0.0001	-2.1938	-4.2446
10	0.0071	0.0001	-2.1487	-4.1996
20	0.0086	0.0001	-2.0655	-4.1163
50	0.0070	0.0001	-2.1549	-4.2057
100	0.0065	0.0001	-2.1871	-4.2379
L/S	Li			
	MW	6.911		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.1451	0.0210	-0.8383	-1.6779
1	0.1290	0.0187	-0.8895	-1.7291
5	0.0663	0.0096	-1.1784	-2.0179
10	0.0138	0.0020	-1.8589	-2.6984
20	0.0401	0.0058	-1.3966	-2.2362
50	0.0279	0.0040	-1.5552	-2.3947
100	0.0070	0.0010	-2.1561	-2.9957
L/S	Pb			
	MW	207.2		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.2764	0.0013	-0.5585	-2.8749
1	0.2541	0.0012	-0.5951	-2.9114
5	0.2668	0.0013	-0.5738	-2.8902
10	0.2386	0.0012	-0.6223	-2.9387
20	0.3015	0.0015	-0.5207	-2.8371
50	0.2130	0.0010	-0.6716	-2.9880
100	0.2334	0.0011	-0.6320	-2.9483

Table D-4 The PW test results of M2 (Chromium, Magnesium, and Vanadium)

L/S	Cr 267.716			
	MW	51.9951		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.9323	0.0179	-0.0304	-1.7464
1	0.8751	0.0168	-0.0579	-1.7739
5	0.8452	0.0163	-0.0730	-1.7890
10	0.9399	0.0181	-0.0269	-1.7429
20	0.8327	0.0160	-0.0795	-1.7955
50	0.9857	0.0190	-0.0063	-1.7222
100	0.8692	0.0167	-0.0609	-1.7769
L/S	Mg			
	MW	24.305		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0413	0.0017	-1.3843	-2.7700
1	0.0441	0.0018	-1.3558	-2.7415
5	0.0173	0.0007	-1.7612	-3.1469
10	0.0126	0.0005	-1.8983	-3.2839
20	0.0204	0.0008	-1.6914	-3.0771
50	0.0098	0.0004	-2.0110	-3.3967
100	0.0055	0.0002	-2.2617	-3.6474
L/S	V			
	MW	50.9415		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0046	0.0000	-2.3391	-8.0462
1	0.0917	0.0000	-1.0378	-6.7449
5	0.1747	0.0000	-0.7578	-6.4649
10	0.0043	0.0000	-2.3696	-8.0766
20	0.0098	0.0000	-2.0101	-7.7172
50	0.0511	0.0000	-1.2915	-6.9986
100	0.0038	0.0000	-2.4179	-8.1250

Table D-5 The PW test results of M2 (Copper, Manganese, and Zinc)

L/S	Cu			
	MW	63.546		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.1117	0.0018	-0.9519	-2.7550
1	0.1059	0.0017	-0.9750	-2.7781
5	0.1010	0.0016	-0.9958	-2.7989
10	0.1076	0.0017	-0.9681	-2.7712
20	0.1040	0.0016	-0.9830	-2.7861
50	0.1105	0.0017	-0.9566	-2.7597
100	0.1010	0.0016	-0.9957	-2.7988
L/S	Mn			
	MW	54.93805		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0089	0.0002	-2.0522	-3.7920
1	0.0071	0.0001	-2.1466	-3.8865
5	0.0093	0.0002	-2.0301	-3.7699
10	0.0101	0.0002	-1.9938	-3.7337
20	0.0087	0.0002	-2.0625	-3.8023
50	0.0088	0.0002	-2.0548	-3.7947
100	0.0098	0.0002	-2.0103	-3.7502
L/S	Zn			
	MW	65.39		
	mg/L	mol/L	log(mg/L)	log(mol/L)
0.5	0.0883	0.0014	-1.0538	-2.8694
1	0.0507	0.0008	-1.2949	-3.1104
5	0.0536	0.0008	-1.2706	-3.0861
10	0.0364	0.0006	-1.4388	-3.2543
20	0.0400	0.0006	-1.3984	-3.2139
50	0.0302	0.0005	-1.5198	-3.3353
100	0.0548	0.0008	-1.2616	-3.0771

APPENDIX E

ANC results

Table E-1 The ANC result of M2 mortar (Alumina Calcium, and Cadmium)

pH (after)	Al	mol/L	log (mol/L)	Ca	mol/L	log (mol/L)	Cd	mol/L	log (mol/L)
12.61	6.254	2.32E-04	-3.63E+00	511.280	1.28E-02	-1.89E+00	12.61	6.254	2.32E-04
12.61	6.849	2.54E-04	-3.60E+00	510.220	1.27E-02	-1.90E+00	12.61	6.849	2.54E-04
12.59	6.468	2.40E-04	-3.62E+00	556.170	1.39E-02	-1.86E+00	12.59	6.468	2.40E-04
12.58	8.108	3.00E-04	-3.52E+00	536.370	1.34E-02	-1.87E+00	12.58	8.108	3.00E-04
12.55	6.601	2.45E-04	-3.61E+00	563.170	1.41E-02	-1.85E+00	12.55	6.601	2.45E-04
12.54	5.828	2.16E-04	-3.67E+00	591.010	1.47E-02	-1.83E+00	12.54	5.828	2.16E-04
12.51	6.480	2.40E-04	-3.62E+00	582.820	1.45E-02	-1.84E+00	12.51	6.480	2.40E-04
12.47	7.876	2.92E-04	-3.53E+00	576.990	1.44E-02	-1.84E+00	12.47	7.876	2.92E-04
12.46	5.445	2.02E-04	-3.70E+00	615.070	1.53E-02	-1.81E+00	12.46	5.445	2.02E-04
12.42	7.206	2.67E-04	-3.57E+00	634.840	1.58E-02	-1.80E+00	12.42	7.206	2.67E-04
12.41	6.226	2.31E-04	-3.64E+00	642.780	1.60E-02	-1.79E+00	12.41	6.226	2.31E-04
12.39	3.128	1.16E-04	-3.94E+00	476.890	1.19E-02	-1.92E+00	12.39	3.128	1.16E-04
12.36	3.927	1.46E-04	-3.84E+00	633.970	1.58E-02	-1.80E+00	12.36	3.927	1.46E-04
12.35	5.521	2.05E-04	-3.69E+00	603.740	1.51E-02	-1.82E+00	12.35	5.521	2.05E-04
12.34	5.828	2.16E-04	-3.67E+00	619.690	1.55E-02	-1.81E+00	12.34	5.828	2.16E-04
12.09	6.479	2.40E-04	-3.62E+00	652.060	1.63E-02	-1.79E+00	12.09	6.479	2.40E-04
12.04	7.924	2.94E-04	-3.53E+00	648.460	1.62E-02	-1.79E+00	12.04	7.924	2.94E-04
12.02	9.596	3.56E-04	-3.45E+00	654.600	1.63E-02	-1.79E+00	12.02	9.596	3.56E-04
11.98	6.561	2.43E-04	-3.61E+00	648.590	1.62E-02	-1.79E+00	11.98	6.561	2.43E-04
11.97	6.567	2.43E-04	-3.61E+00	627.440	1.57E-02	-1.81E+00	11.97	6.567	2.43E-04
11.95	6.729	2.49E-04	-3.60E+00	651.200	1.62E-02	-1.79E+00	11.95	6.729	2.49E-04
11.91	10.773	3.99E-04	-3.40E+00	675.880	1.69E-02	-1.77E+00	11.91	10.773	3.99E-04
11.9	8.727	3.23E-04	-3.49E+00	680.130	1.70E-02	-1.77E+00	11.9	8.727	3.23E-04
11.88	7.597	2.82E-04	-3.55E+00	658.820	1.64E-02	-1.78E+00	11.88	7.597	2.82E-04
11.85	10.380	3.85E-04	-3.41E+00	661.950	1.65E-02	-1.78E+00	11.85	10.380	3.85E-04
11.81	6.539	2.42E-04	-3.62E+00	660.700	1.65E-02	-1.78E+00	11.81	6.539	2.42E-04
11.77	11.446	4.24E-04	-3.37E+00	683.030	1.70E-02	-1.77E+00	11.77	11.446	4.24E-04
11.7	11.680	4.33E-04	-3.36E+00	694.300	1.73E-02	-1.76E+00	11.7	11.680	4.33E-04
11.69	11.191	4.15E-04	-3.38E+00	700.970	1.75E-02	-1.76E+00	11.69	11.191	4.15E-04
11.63	8.843	3.28E-04	-3.48E+00	706.960	1.76E-02	-1.75E+00	11.63	8.843	3.28E-04
11.6	8.122	3.01E-04	-3.52E+00	700.030	1.75E-02	-1.76E+00	11.6	8.122	3.01E-04
11.46	8.041	2.98E-04	-3.53E+00	709.260	1.77E-02	-1.75E+00	11.46	8.041	2.98E-04
11.42	2.930	1.09E-04	-3.96E+00	691.540	1.73E-02	-1.76E+00	11.42	2.930	1.09E-04
11.32	9.434	3.50E-04	-3.46E+00	722.070	1.80E-02	-1.74E+00	11.32	9.434	3.50E-04
11.29	2.047	7.59E-05	-4.12E+00	691.200	1.72E-02	-1.76E+00	11.29	2.047	7.59E-05
11.27	3.069	1.14E-04	-3.94E+00	697.740	1.74E-02	-1.76E+00	11.27	3.069	1.14E-04
11.16	5.167	1.91E-04	-3.72E+00	719.000	1.79E-02	-1.75E+00	11.16	5.167	1.91E-04
11.09	4.265	1.58E-04	-3.80E+00	723.500	1.81E-02	-1.74E+00	11.09	4.265	1.58E-04
11.05	1.746	6.47E-05	-4.19E+00	720.410	1.80E-02	-1.75E+00	11.05	1.746	6.47E-05
11.04	4.759	1.76E-04	-3.75E+00	724.320	1.81E-02	-1.74E+00	11.04	4.759	1.76E-04
11.03	1.800	6.67E-05	-4.18E+00	720.930	1.80E-02	-1.75E+00	11.03	1.800	6.67E-05
11.01	5.381	1.99E-04	-3.70E+00	726.420	1.81E-02	-1.74E+00	11.01	5.381	1.99E-04
10.97	1.888	7.00E-05	-4.16E+00	718.550	1.79E-02	-1.75E+00	10.97	1.888	7.00E-05
10.83	1.973	7.31E-05	-4.14E+00	734.320	1.83E-02	-1.74E+00	10.83	1.973	7.31E-05
10.79	4.623	1.71E-04	-3.77E+00	670.520	1.67E-02	-1.78E+00	10.79	4.623	1.71E-04
10.75	2.764	1.02E-04	-3.99E+00	732.750	1.83E-02	-1.74E+00	10.75	2.764	1.02E-04
10.72	4.365	1.62E-04	-3.79E+00	741.270	1.85E-02	-1.73E+00	10.72	4.365	1.62E-04
10.61	5.036	1.87E-04	-3.73E+00	726.460	1.81E-02	-1.74E+00	10.61	5.036	1.87E-04
10.59	1.502	5.57E-05	-4.25E+00	738.600	1.84E-02	-1.73E+00	10.59	1.502	5.57E-05
10.52	6.772	2.51E-04	-3.60E+00	739.240	1.84E-02	-1.73E+00	10.52	6.772	2.51E-04
10.34	5.599	2.08E-04	-3.68E+00	750.780	1.87E-02	-1.73E+00	10.34	5.599	2.08E-04
10.31	5.777	2.14E-04	-3.67E+00	743.080	1.85E-02	-1.73E+00	10.31	5.777	2.14E-04
10.21	7.529	2.79E-04	-3.55E+00	746.360	1.86E-02	-1.73E+00	10.21	7.529	2.79E-04
10.08	2.762	1.02E-04	-3.99E+00	747.360	1.86E-02	-1.73E+00	10.08	2.762	1.02E-04
10.03	5.482	2.03E-04	-3.69E+00	762.270	1.90E-02	-1.72E+00	10.03	5.482	2.03E-04
9.45	3.721	1.38E-04	-3.86E+00	762.000	1.90E-02	-1.72E+00	9.45	3.721	1.38E-04
9.33	3.367	1.25E-04	-3.90E+00	757.980	1.89E-02	-1.72E+00	9.33	3.367	1.25E-04
9.11	2.730	1.01E-04	-3.99E+00	761.840	1.90E-02	-1.72E+00	9.11	2.730	1.01E-04
9	3.619	1.34E-04	-3.87E+00	757.100	1.89E-02	-1.72E+00	9	3.619	1.34E-04
8.72	4.482	1.66E-04	-3.78E+00	755.400	1.88E-02	-1.72E+00	8.72	4.482	1.66E-04
8.48	7.891	2.92E-04	-3.53E+00	767.250	1.91E-02	-1.72E+00	8.48	7.891	2.92E-04
7.12	3.164	1.17E-04	-3.93E+00	762.170	1.90E-02	-1.72E+00	7.12	3.164	1.17E-04
7.06	1.701	6.30E-05	-4.20E+00	765.350	1.91E-02	-1.72E+00	7.06	1.701	6.30E-05
6.4	11.117	4.12E-04	-3.39E+00	778.220	1.94E-02	-1.71E+00	6.4	11.117	4.12E-04
5.82	18.684	6.92E-04	-3.16E+00	772.370	1.93E-02	-1.72E+00	5.82	18.684	6.92E-04
1.12	449.760	1.67E-02	-1.78E+00	768.200	1.92E-02	-1.72E+00	1.12	449.760	1.67E-02

Table E-2 The ANC result of M2 mortar (Chromium, Copper and iron)

pH (after)	Cr	mol/L	log (mol/L)	Cu	mol/L	log (mol/L)	Fe	mol/L	log (mol/L)
12.61	0.775	1.49E-05	-4.83E+00	0.050	7.90E-07	-6.10E+00	4.889	8.75E-05	-4.06E+00
12.61	0.793	1.52E-05	-4.82E+00	0.047	7.34E-07	-6.13E+00	5.810	1.04E-04	-3.98E+00
12.59	0.819	1.58E-05	-4.80E+00	0.031	4.88E-07	-6.31E+00	5.325	9.54E-05	-4.02E+00
12.58	0.790	1.52E-05	-4.82E+00	0.075	1.18E-06	-5.93E+00	6.246	1.12E-04	-3.95E+00
12.55	0.764	1.47E-05	-4.83E+00	0.043	6.77E-07	-6.17E+00	4.972	8.90E-05	-4.05E+00
12.54	0.748	1.44E-05	-4.84E+00	0.037	5.74E-07	-6.24E+00	4.439	7.95E-05	-4.10E+00
12.51	0.757	1.46E-05	-4.84E+00	0.034	5.42E-07	-6.27E+00	5.172	9.26E-05	-4.03E+00
12.47	0.815	1.57E-05	-4.80E+00	0.056	8.87E-07	-6.05E+00	8.069	1.44E-04	-3.84E+00
12.46	0.884	1.70E-05	-4.77E+00	0.041	6.51E-07	-6.19E+00	4.439	7.95E-05	-4.10E+00
12.42	0.970	1.87E-05	-4.73E+00	0.038	5.98E-07	-6.22E+00	8.611	1.54E-04	-3.81E+00
12.41	0.735	1.41E-05	-4.85E+00	0.035	5.43E-07	-6.27E+00	4.330	7.75E-05	-4.11E+00
12.39	0.497	9.56E-06	-5.02E+00	0.038	6.05E-07	-6.22E+00	2.917	5.22E-05	-4.28E+00
12.36	0.976	1.88E-05	-4.73E+00	0.032	5.07E-07	-6.29E+00	2.539	4.55E-05	-4.34E+00
12.35	1.224	2.35E-05	-4.63E+00	0.037	5.79E-07	-6.24E+00	6.307	1.13E-04	-3.95E+00
12.34	0.941	1.81E-05	-4.74E+00	0.037	5.75E-07	-6.24E+00	7.469	1.34E-04	-3.87E+00
12.09	0.974	1.87E-05	-4.73E+00	0.030	4.65E-07	-6.33E+00	6.309	1.13E-04	-3.95E+00
12.04	1.081	2.08E-05	-4.68E+00	0.033	5.14E-07	-6.29E+00	7.537	1.35E-04	-3.87E+00
12.02	1.247	2.40E-05	-4.62E+00	0.053	8.38E-07	-6.08E+00	10.564	1.89E-04	-3.72E+00
11.98	1.289	2.48E-05	-4.61E+00	0.031	4.87E-07	-6.31E+00	7.105	1.27E-04	-3.90E+00
11.97	0.936	1.80E-05	-4.74E+00	0.034	5.36E-07	-6.27E+00	6.603	1.18E-04	-3.93E+00
11.95	1.306	2.51E-05	-4.60E+00	0.045	7.06E-07	-6.15E+00	6.478	1.16E-04	-3.94E+00
11.91	1.834	3.53E-05	-4.45E+00	0.094	1.48E-06	-5.83E+00	23.483	4.21E-04	-3.38E+00
11.9	1.593	3.06E-05	-4.51E+00	0.036	5.63E-07	-6.25E+00	8.622	1.54E-04	-3.81E+00
11.88	1.740	3.35E-05	-4.48E+00	0.027	4.21E-07	-6.38E+00	8.036	1.44E-04	-3.84E+00
11.85	1.650	3.17E-05	-4.50E+00	0.041	6.38E-07	-6.19E+00	11.451	2.05E-04	-3.69E+00
11.81	2.228	4.29E-05	-4.37E+00	0.038	6.04E-07	-6.22E+00	8.742	1.57E-04	-3.81E+00
11.77	2.102	4.04E-05	-4.39E+00	0.049	7.72E-07	-6.11E+00	12.420	2.22E-04	-3.65E+00
11.7	2.110	4.06E-05	-4.39E+00	0.047	7.39E-07	-6.13E+00	12.854	2.30E-04	-3.64E+00
11.69	2.160	4.15E-05	-4.38E+00	0.055	8.68E-07	-6.06E+00	13.878	2.49E-04	-3.60E+00
11.63	2.356	4.53E-05	-4.34E+00	0.041	6.49E-07	-6.19E+00	9.926	1.78E-04	-3.75E+00
11.6	2.508	4.82E-05	-4.32E+00	0.035	5.51E-07	-6.26E+00	9.070	1.62E-04	-3.79E+00
11.46	3.209	6.17E-05	-4.21E+00	0.024	3.79E-07	-6.42E+00	8.821	1.58E-04	-3.80E+00
11.42	4.024	7.74E-05	-4.11E+00	0.015	2.35E-07	-6.63E+00	2.931	5.25E-05	-4.28E+00
11.32	3.730	7.17E-05	-4.14E+00	0.045	7.07E-07	-6.15E+00	11.420	2.04E-04	-3.69E+00
11.29	3.354	6.45E-05	-4.19E+00	0.007	1.07E-07	-6.97E+00	2.932	5.25E-05	-4.28E+00
11.27	3.513	6.76E-05	-4.17E+00	0.028	4.41E-07	-6.36E+00	6.340	1.14E-04	-3.94E+00
11.16	4.593	8.83E-05	-4.05E+00	0.020	3.12E-07	-6.51E+00	5.641	1.01E-04	-4.00E+00
11.09	4.730	9.10E-05	-4.04E+00	0.034	5.34E-07	-6.27E+00	4.679	8.38E-05	-4.08E+00
11.05	5.571	1.07E-04	-3.97E+00	0.009	1.49E-07	-6.83E+00	2.125	3.81E-05	-4.42E+00
11.04	5.059	9.73E-05	-4.01E+00	0.020	3.15E-07	-6.50E+00	5.804	1.04E-04	-3.98E+00
11.03	5.615	1.08E-04	-3.97E+00	0.021	3.23E-07	-6.49E+00	3.031	5.43E-05	-4.27E+00
11.01	5.402	1.04E-04	-3.98E+00	0.037	5.83E-07	-6.23E+00	6.368	1.14E-04	-3.94E+00
10.97	5.662	1.09E-04	-3.96E+00	0.035	5.49E-07	-6.26E+00	7.097	1.27E-04	-3.90E+00
10.83	6.669	1.28E-04	-3.89E+00	0.008	1.28E-07	-6.89E+00	2.181	3.91E-05	-4.41E+00
10.79	2.332	4.48E-05	-4.35E+00	0.019	2.97E-07	-6.53E+00	4.619	8.27E-05	-4.08E+00
10.75	6.394	1.23E-04	-3.91E+00	0.014	2.21E-07	-6.66E+00	3.084	5.52E-05	-4.26E+00
10.72	6.605	1.27E-04	-3.90E+00	0.025	3.88E-07	-6.41E+00	5.476	9.81E-05	-4.01E+00
10.61	5.767	1.11E-04	-3.96E+00	0.031	4.84E-07	-6.31E+00	6.045	1.08E-04	-3.97E+00
10.59	9.004	1.73E-04	-3.76E+00	0.031	4.91E-07	-6.31E+00	1.418	2.54E-05	-4.60E+00
10.52	8.558	1.65E-04	-3.78E+00	0.027	4.28E-07	-6.37E+00	11.543	2.07E-04	-3.68E+00
10.34	9.209	1.77E-04	-3.75E+00	0.033	5.22E-07	-6.28E+00	9.160	1.64E-04	-3.79E+00
10.31	10.213	1.96E-04	-3.71E+00	0.009	1.47E-07	-6.83E+00	8.683	1.55E-04	-3.81E+00
10.21	8.818	1.70E-04	-3.77E+00	0.043	6.77E-07	-6.17E+00	13.989	2.50E-04	-3.60E+00
10.08	7.244	1.39E-04	-3.86E+00	0.006	9.96E-08	-7.00E+00	3.047	5.46E-05	-4.26E+00
10.03	9.579	1.84E-04	-3.73E+00	0.030	4.80E-07	-6.32E+00	9.488	1.70E-04	-3.77E+00
9.45	11.579	2.23E-04	-3.65E+00	0.013	2.02E-07	-6.69E+00	6.198	1.11E-04	-3.95E+00
9.33	11.974	2.30E-04	-3.64E+00	0.010	1.52E-07	-6.82E+00	5.728	1.03E-04	-3.99E+00
9.11	10.572	2.03E-04	-3.69E+00	0.024	3.77E-07	-6.42E+00	4.307	7.71E-05	-4.11E+00
9	11.260	2.17E-04	-3.66E+00	0.015	2.35E-07	-6.63E+00	6.768	1.21E-04	-3.92E+00
8.72	12.573	2.42E-04	-3.62E+00	0.010	1.54E-07	-6.81E+00	8.023	1.44E-04	-3.84E+00
8.48	12.571	2.42E-04	-3.62E+00	0.053	8.29E-07	-6.08E+00	19.882	3.56E-04	-3.45E+00
7.12	11.758	2.26E-04	-3.65E+00	0.001	9.13E-09	-8.04E+00	5.307	9.50E-05	-4.02E+00
7.06	13.046	2.51E-04	-3.60E+00	0.009	1.39E-07	-6.86E+00	2.301	4.12E-05	-4.39E+00
6.4	11.967	2.30E-04	-3.64E+00	0.051	8.03E-07	-6.10E+00	20.106	3.60E-04	-3.44E+00
5.82	10.203	1.96E-04	-3.71E+00	0.141	2.21E-06	-5.65E+00	33.448	5.99E-04	-3.22E+00
1.12	17.927	3.45E-04	-3.46E+00	2.163	3.40E-05	-4.47E+00	775.610	1.39E-02	-1.86E+00

Table E-3 The ANC result of M2 mortar (Potassium, Lithium, and Magnesium)

pH (after)	K	mol/L	log (mol/L)	Li	mol/L	log (mol/L)	Mg	mol/L	log (mol/L)
12.61	35.365	9.05E-04	-3.04E+00	0.078	1.13E-05	-4.95E+00	4.290	1.77E-04	-3.75E+00
12.61	38.239	9.78E-04	-3.01E+00	0.084	1.22E-05	-4.91E+00	4.956	2.04E-04	-3.69E+00
12.59	36.178	9.25E-04	-3.03E+00	0.079	1.15E-05	-4.94E+00	4.307	1.77E-04	-3.75E+00
12.58	35.014	8.96E-04	-3.05E+00	0.078	1.13E-05	-4.95E+00	3.034	1.25E-04	-3.90E+00
12.55	32.666	8.35E-04	-3.08E+00	0.072	1.05E-05	-4.98E+00	2.875	1.18E-04	-3.93E+00
12.54	32.320	8.27E-04	-3.08E+00	0.069	9.98E-06	-5.00E+00	3.216	1.32E-04	-3.88E+00
12.51	32.096	8.21E-04	-3.09E+00	0.072	1.04E-05	-4.98E+00	2.895	1.19E-04	-3.92E+00
12.47	30.931	7.91E-04	-3.10E+00	0.071	1.02E-05	-4.99E+00	3.497	1.44E-04	-3.84E+00
12.46	34.540	8.83E-04	-3.05E+00	0.077	1.11E-05	-4.95E+00	2.231	9.18E-05	-4.04E+00
12.42	38.633	9.88E-04	-3.01E+00	0.091	1.31E-05	-4.88E+00	3.873	1.59E-04	-3.80E+00
12.41	30.757	7.87E-04	-3.10E+00	0.063	9.05E-06	-5.04E+00	2.883	1.19E-04	-3.93E+00
12.39	22.314	5.71E-04	-3.24E+00	0.051	7.44E-06	-5.13E+00	2.968	1.22E-04	-3.91E+00
12.36	37.702	9.64E-04	-3.02E+00	0.084	1.21E-05	-4.92E+00	1.688	6.95E-05	-4.16E+00
12.35	34.741	8.89E-04	-3.05E+00	0.074	1.07E-05	-4.97E+00	3.428	1.41E-04	-3.85E+00
12.34	34.187	8.74E-04	-3.06E+00	0.093	1.34E-05	-4.87E+00	2.747	1.13E-04	-3.95E+00
12.09	33.369	8.53E-04	-3.07E+00	0.079	1.14E-05	-4.94E+00	2.270	9.34E-05	-4.03E+00
12.04	36.535	9.34E-04	-3.03E+00	0.083	1.20E-05	-4.92E+00	3.158	1.30E-04	-3.89E+00
12.02	36.300	9.28E-04	-3.03E+00	0.086	1.24E-05	-4.91E+00	3.882	1.60E-04	-3.80E+00
11.98	34.950	8.94E-04	-3.05E+00	0.084	1.22E-05	-4.91E+00	2.973	1.22E-04	-3.91E+00
11.97	29.790	7.62E-04	-3.12E+00	0.078	1.13E-05	-4.95E+00	2.471	1.02E-04	-3.99E+00
11.95	34.282	8.77E-04	-3.06E+00	0.084	1.22E-05	-4.91E+00	3.511	1.44E-04	-3.84E+00
11.91	41.338	1.06E-03	-2.98E+00	0.081	1.17E-05	-4.93E+00	4.925	2.03E-04	-3.69E+00
11.9	40.706	1.04E-03	-2.98E+00	0.094	1.37E-05	-4.86E+00	3.429	1.41E-04	-3.85E+00
11.88	35.316	9.03E-04	-3.04E+00	0.087	1.26E-05	-4.90E+00	3.253	1.34E-04	-3.87E+00
11.85	35.263	9.02E-04	-3.04E+00	0.089	1.29E-05	-4.89E+00	4.024	1.66E-04	-3.78E+00
11.81	32.643	8.35E-04	-3.08E+00	0.084	1.22E-05	-4.91E+00	3.714	1.53E-04	-3.82E+00
11.77	39.223	1.00E-03	-3.00E+00	0.096	1.38E-05	-4.86E+00	4.029	1.66E-04	-3.78E+00
11.7	41.202	1.05E-03	-2.98E+00	0.102	1.48E-05	-4.83E+00	4.749	1.95E-04	-3.71E+00
11.69	41.880	1.07E-03	-2.97E+00	0.102	1.48E-05	-4.83E+00	4.540	1.87E-04	-3.73E+00
11.63	41.547	1.06E-03	-2.97E+00	0.102	1.48E-05	-4.83E+00	3.676	1.51E-04	-3.82E+00
11.6	39.313	1.01E-03	-3.00E+00	0.098	1.42E-05	-4.85E+00	3.095	1.27E-04	-3.89E+00
11.46	40.540	1.04E-03	-2.98E+00	0.106	1.53E-05	-4.82E+00	3.003	1.24E-04	-3.91E+00
11.42	36.705	9.39E-04	-3.03E+00	0.093	1.35E-05	-4.87E+00	2.576	1.06E-04	-3.97E+00
11.32	42.668	1.09E-03	-2.96E+00	0.112	1.63E-05	-4.79E+00	3.271	1.35E-04	-3.87E+00
11.29	32.269	8.25E-04	-3.08E+00	0.090	1.30E-05	-4.89E+00	1.797	7.39E-05	-4.13E+00
11.27	34.299	8.77E-04	-3.06E+00	0.100	1.45E-05	-4.84E+00	2.399	9.87E-05	-4.01E+00
11.16	39.811	1.02E-03	-2.99E+00	0.111	1.60E-05	-4.80E+00	2.805	1.15E-04	-3.94E+00
11.09	38.922	9.95E-04	-3.00E+00	0.109	1.58E-05	-4.80E+00	1.750	7.20E-05	-4.14E+00
11.05	37.732	9.65E-04	-3.02E+00	0.109	1.57E-05	-4.80E+00	1.963	8.08E-05	-4.09E+00
11.04	38.847	9.94E-04	-3.00E+00	0.112	1.62E-05	-4.79E+00	2.229	9.17E-05	-4.04E+00
11.03	41.373	1.06E-03	-2.98E+00	0.117	1.69E-05	-4.77E+00	1.513	6.22E-05	-4.21E+00
11.01	41.738	1.07E-03	-2.97E+00	0.117	1.69E-05	-4.77E+00	2.764	1.14E-04	-3.94E+00
10.97	38.927	9.96E-04	-3.00E+00	0.111	1.60E-05	-4.80E+00	1.532	6.30E-05	-4.20E+00
10.83	37.979	9.71E-04	-3.01E+00	0.116	1.68E-05	-4.77E+00	1.162	4.78E-05	-4.32E+00
10.79	35.402	9.05E-04	-3.04E+00	0.089	1.29E-05	-4.89E+00	2.549	1.05E-04	-3.98E+00
10.75	39.303	1.01E-03	-3.00E+00	0.114	1.64E-05	-4.78E+00	1.919	7.89E-05	-4.10E+00
10.72	40.106	1.03E-03	-2.99E+00	0.121	1.75E-05	-4.76E+00	2.152	8.85E-05	-4.05E+00
10.61	41.221	1.05E-03	-2.98E+00	0.117	1.69E-05	-4.77E+00	2.192	9.02E-05	-4.04E+00
10.59	47.148	1.21E-03	-2.92E+00	0.132	1.92E-05	-4.72E+00	1.591	6.54E-05	-4.18E+00
10.52	38.225	9.78E-04	-3.01E+00	0.122	1.77E-05	-4.75E+00	3.077	1.27E-04	-3.90E+00
10.34	39.194	1.00E-03	-3.00E+00	0.135	1.96E-05	-4.71E+00	2.925	1.20E-04	-3.92E+00
10.31	45.712	1.17E-03	-2.93E+00	0.151	2.19E-05	-4.66E+00	2.698	1.11E-04	-3.95E+00
10.21	71.207	1.82E-03	-2.74E+00	0.137	1.99E-05	-4.70E+00	4.018	1.65E-04	-3.78E+00
10.08	39.537	1.01E-03	-3.00E+00	0.124	1.79E-05	-4.75E+00	1.511	6.22E-05	-4.21E+00
10.03	41.078	1.05E-03	-2.98E+00	0.141	2.04E-05	-4.69E+00	2.503	1.03E-04	-3.99E+00
9.45	45.978	1.18E-03	-2.93E+00	0.204	2.96E-05	-4.53E+00	8.046	3.31E-04	-3.48E+00
9.33	47.804	1.22E-03	-2.91E+00	0.218	3.16E-05	-4.50E+00	12.080	4.97E-04	-3.30E+00
9.11	46.073	1.18E-03	-2.93E+00	0.207	2.99E-05	-4.52E+00	15.129	6.22E-04	-3.21E+00
9	43.442	1.11E-03	-2.95E+00	0.228	3.30E-05	-4.48E+00	37.042	1.52E-03	-2.82E+00
8.72	44.591	1.14E-03	-2.94E+00	0.206	2.98E-05	-4.53E+00	8.112	3.34E-04	-3.48E+00
8.48	49.220	1.26E-03	-2.90E+00	0.337	4.88E-05	-4.31E+00	153.210	6.30E-03	-2.20E+00
7.12	43.562	1.11E-03	-2.95E+00	0.210	3.04E-05	-4.52E+00	12.640	5.20E-04	-3.28E+00
7.06	47.501	1.21E-03	-2.92E+00	0.320	4.63E-05	-4.33E+00	129.740	5.34E-03	-2.27E+00
6.4	64.616	1.65E-03	-2.78E+00	0.341	4.93E-05	-4.31E+00	160.420	6.60E-03	-2.18E+00
5.82	50.803	1.30E-03	-2.89E+00	0.338	4.89E-05	-4.31E+00	159.710	6.57E-03	-2.18E+00
1.12	68.317	1.75E-03	-2.76E+00	0.411	5.95E-05	-4.23E+00	187.140	7.70E-03	-2.11E+00

Table E-4 The ANC result of M2 mortar (Manganese, Sodium, and Nickel)

pH (after)	Mn	mol/L	log (mol/L)	Na	mol/L	log (mol/L)	Ni	mol/L	log (mol/L)
12.61	0.103	1.88E-06	-5.73E+00	27.708	1.21E-03	-2.92E+00	0.052	8.86E-07	-6.05E+00
12.61	0.122	2.23E-06	-5.65E+00	30.383	1.32E-03	-2.88E+00	0.111	1.90E-06	-5.72E+00
12.59	0.124	2.25E-06	-5.65E+00	27.246	1.19E-03	-2.93E+00	0.057	9.63E-07	-6.02E+00
12.58	0.140	2.56E-06	-5.59E+00	23.735	1.03E-03	-2.99E+00	0.041	6.92E-07	-6.16E+00
12.55	0.120	2.19E-06	-5.66E+00	21.740	9.46E-04	-3.02E+00	0.054	9.27E-07	-6.03E+00
12.54	0.101	1.84E-06	-5.73E+00	22.893	9.96E-04	-3.00E+00	0.023	3.98E-07	-6.40E+00
12.51	0.117	2.14E-06	-5.67E+00	21.034	9.15E-04	-3.04E+00	0.064	1.09E-06	-5.96E+00
12.47	0.187	3.41E-06	-5.47E+00	22.918	9.97E-04	-3.00E+00	0.074	1.25E-06	-5.90E+00
12.46	0.109	1.98E-06	-5.70E+00	21.830	9.50E-04	-3.02E+00	0.038	6.40E-07	-6.19E+00
12.42	0.177	3.23E-06	-5.49E+00	25.238	1.10E-03	-2.96E+00	0.127	2.17E-06	-5.66E+00
12.41	0.099	1.81E-06	-5.74E+00	33.373	1.45E-03	-2.84E+00	0.063	1.07E-06	-5.97E+00
12.39	0.070	1.27E-06	-5.90E+00	24.429	1.06E-03	-2.97E+00	0.040	6.80E-07	-6.17E+00
12.36	0.061	1.11E-06	-5.95E+00	23.617	1.03E-03	-2.99E+00	0.028	4.71E-07	-6.33E+00
12.35	0.141	2.57E-06	-5.59E+00	112.970	4.91E-03	-2.31E+00	0.100	1.70E-06	-5.77E+00
12.34	0.122	2.22E-06	-5.65E+00	22.391	9.74E-04	-3.01E+00	0.170	2.89E-06	-5.54E+00
12.09	0.139	2.52E-06	-5.60E+00	21.178	9.21E-04	-3.04E+00	0.052	8.91E-07	-6.05E+00
12.04	0.176	3.20E-06	-5.49E+00	32.784	1.43E-03	-2.85E+00	0.044	7.52E-07	-6.12E+00
12.02	0.220	4.01E-06	-5.40E+00	54.956	2.39E-03	-2.62E+00	0.068	1.16E-06	-5.93E+00
11.98	0.179	3.27E-06	-5.49E+00	22.394	9.74E-04	-3.01E+00	0.051	8.61E-07	-6.07E+00
11.97	0.135	2.45E-06	-5.61E+00	18.282	7.95E-04	-3.10E+00	0.032	5.51E-07	-6.26E+00
11.95	0.184	3.35E-06	-5.48E+00	25.145	1.09E-03	-2.96E+00	0.041	7.01E-07	-6.15E+00
11.91	0.391	7.11E-06	-5.15E+00	128.180	5.58E-03	-2.25E+00	0.152	2.60E-06	-5.59E+00
11.9	0.188	3.43E-06	-5.47E+00	22.954	9.98E-04	-3.00E+00	0.055	9.30E-07	-6.03E+00
11.88	0.174	3.17E-06	-5.50E+00	20.772	9.04E-04	-3.04E+00	0.043	7.26E-07	-6.14E+00
11.85	0.249	4.54E-06	-5.34E+00	19.930	8.67E-04	-3.06E+00	0.033	5.64E-07	-6.25E+00
11.81	0.207	3.76E-06	-5.42E+00	21.337	9.28E-04	-3.03E+00	0.040	6.77E-07	-6.17E+00
11.77	0.272	4.95E-06	-5.31E+00	21.878	9.52E-04	-3.02E+00	0.048	8.24E-07	-6.08E+00
11.7	0.279	5.08E-06	-5.29E+00	24.717	1.08E-03	-2.97E+00	0.065	1.11E-06	-5.96E+00
11.69	0.297	5.40E-06	-5.27E+00	26.727	1.16E-03	-2.93E+00	0.060	1.02E-06	-5.99E+00
11.63	0.218	3.96E-06	-5.40E+00	22.550	9.81E-04	-3.01E+00	0.044	7.55E-07	-6.12E+00
11.6	0.195	3.55E-06	-5.45E+00	26.542	1.15E-03	-2.94E+00	0.029	4.94E-07	-6.31E+00
11.46	0.194	3.52E-06	-5.45E+00	24.220	1.05E-03	-2.98E+00	0.045	7.75E-07	-6.11E+00
11.42	0.059	1.07E-06	-5.97E+00	27.506	1.20E-03	-2.92E+00	0.021	3.58E-07	-6.45E+00
11.32	0.243	4.43E-06	-5.35E+00	22.497	9.79E-04	-3.01E+00	0.042	7.12E-07	-6.15E+00
11.29	0.058	1.06E-06	-5.98E+00	19.370	8.43E-04	-3.07E+00	0.021	3.55E-07	-6.45E+00
11.27	0.108	1.97E-06	-5.71E+00	20.285	8.82E-04	-3.05E+00	0.087	1.49E-06	-5.83E+00
11.16	0.125	2.28E-06	-5.64E+00	22.855	9.94E-04	-3.00E+00	0.048	8.16E-07	-6.09E+00
11.09	0.103	1.88E-06	-5.73E+00	21.640	9.41E-04	-3.03E+00	0.047	7.95E-07	-6.10E+00
11.05	0.041	7.54E-07	-6.12E+00	24.635	1.07E-03	-2.97E+00	0.043	7.24E-07	-6.14E+00
11.04	0.127	2.30E-06	-5.64E+00	21.016	9.14E-04	-3.04E+00	0.029	4.95E-07	-6.31E+00
11.03	0.059	1.08E-06	-5.97E+00	22.794	9.91E-04	-3.00E+00	0.033	5.55E-07	-6.26E+00
11.01	0.140	2.55E-06	-5.59E+00	24.295	1.06E-03	-2.98E+00	0.047	7.96E-07	-6.10E+00
10.97	0.130	2.37E-06	-5.62E+00	21.142	9.20E-04	-3.04E+00	0.031	5.34E-07	-6.27E+00
10.83	0.047	8.57E-07	-6.07E+00	19.245	8.37E-04	-3.08E+00	0.031	5.29E-07	-6.28E+00
10.79	0.110	2.00E-06	-5.70E+00	20.550	8.94E-04	-3.05E+00	0.018	3.14E-07	-6.50E+00
10.75	0.062	1.14E-06	-5.94E+00	21.363	9.29E-04	-3.03E+00	0.031	5.34E-07	-6.27E+00
10.72	0.115	2.09E-06	-5.68E+00	20.769	9.03E-04	-3.04E+00	0.021	3.65E-07	-6.44E+00
10.61	0.126	2.30E-06	-5.64E+00	22.715	9.88E-04	-3.01E+00	0.046	7.77E-07	-6.11E+00
10.59	0.028	5.05E-07	-6.30E+00	31.762	1.38E-03	-2.86E+00	0.035	5.96E-07	-6.22E+00
10.52	0.216	3.94E-06	-5.40E+00	24.036	1.05E-03	-2.98E+00	0.056	9.62E-07	-6.02E+00
10.34	0.156	2.84E-06	-5.55E+00	22.520	9.80E-04	-3.01E+00	0.026	4.39E-07	-6.36E+00
10.31	0.160	2.92E-06	-5.54E+00	24.247	1.05E-03	-2.98E+00	0.040	6.88E-07	-6.16E+00
10.21	0.250	4.54E-06	-5.34E+00	30.391	1.32E-03	-2.88E+00	0.050	8.52E-07	-6.07E+00
10.08	0.061	1.11E-06	-5.96E+00	20.062	8.73E-04	-3.06E+00	0.035	5.90E-07	-6.23E+00
10.03	0.160	2.90E-06	-5.54E+00	20.846	9.07E-04	-3.04E+00	0.035	6.03E-07	-6.22E+00
9.45	0.118	2.15E-06	-5.67E+00	47.311	2.06E-03	-2.69E+00	0.040	6.77E-07	-6.17E+00
9.33	0.137	2.50E-06	-5.60E+00	23.806	1.04E-03	-2.98E+00	0.019	3.19E-07	-6.50E+00
9.11	0.090	1.64E-06	-5.78E+00	26.216	1.14E-03	-2.94E+00	0.046	7.83E-07	-6.11E+00
9	0.158	2.87E-06	-5.54E+00	25.951	1.13E-03	-2.95E+00	0.038	6.51E-07	-6.19E+00
8.72	0.165	3.01E-06	-5.52E+00	21.070	9.16E-04	-3.04E+00	0.042	7.19E-07	-6.14E+00
8.48	4.999	9.10E-05		25.903	1.13E-03	-2.95E+00	1.476	2.51E-05	
7.12	0.111	2.02E-06	-5.70E+00	20.365	8.86E-04	-3.05E+00	0.029	5.02E-07	-6.30E+00
7.06	0.113	2.06E-06	-5.69E+00	30.480	1.33E-03	-2.88E+00	0.091	1.54E-06	-5.81E+00
6.4	7.081	1.29E-04	-3.89E+00	24.625	1.07E-03	-2.97E+00	2.233	3.80E-05	-4.42E+00
5.82	7.847	1.43E-04	-3.85E+00	30.602	1.33E-03	-2.88E+00	2.685	4.57E-05	-4.34E+00
1.12	19.238	3.50E-04	-3.46E+00	29.973	1.30E-03	-2.88E+00	3.789	6.46E-05	-4.19E+00

Table E-5 The ANC result of M2 mortar (Vanadium, Zinc, and Lead)

pH (after)	V	mol/L	log (mol/L)	Zn	mol/L	log (mol/L)	Pb	mol/L	log (mol/L)
12.61	0.229	4.50E-06	-5.35E+00	0.412	6.31E-06	-5.20E+00	0.300	1.45E-06	-5.84E+00
12.61	0.349	6.84E-06	-5.16E+00	0.635	9.70E-06	-5.01E+00	0.286	1.38E-06	-5.86E+00
12.59	0.361	7.08E-06	-5.15E+00	0.404	6.18E-06	-5.21E+00	0.153	7.40E-07	-6.13E+00
12.58	0.528	1.04E-05	-4.98E+00	0.266	4.06E-06	-5.39E+00	0.148	7.12E-07	-6.15E+00
12.55	0.534	1.05E-05	-4.98E+00	0.235	3.60E-06	-5.44E+00	0.099	4.79E-07	-6.32E+00
12.54	0.036	7.15E-07	-6.15E+00	0.325	4.97E-06	-5.30E+00	0.113	5.44E-07	-6.26E+00
12.51	0.050	9.79E-07	-6.01E+00	0.412	6.30E-06	-5.20E+00	0.233	1.13E-06	-5.95E+00
12.47	0.059	1.16E-06	-5.94E+00	0.801	1.23E-05	-4.91E+00	0.244	1.18E-06	-5.93E+00
12.46	0.063	1.23E-06	-5.91E+00	0.164	2.51E-06	-5.60E+00	0.114	5.50E-07	-6.26E+00
12.42	0.070	1.38E-06	-5.86E+00	0.236	3.61E-06	-5.44E+00	0.636	3.07E-06	-5.51E+00
12.41	0.063	1.23E-06	-5.91E+00	0.813	1.24E-05	-4.91E+00	0.137	6.61E-07	-6.18E+00
12.39	0.056	1.09E-06	-5.96E+00	0.659	1.01E-05	-5.00E+00	0.150	7.25E-07	-6.14E+00
12.36	0.092	1.81E-06	-5.74E+00	0.148	2.27E-06	-5.64E+00	0.109	5.24E-07	-6.28E+00
12.35	0.491	9.64E-06	-5.02E+00	0.275	4.20E-06	-5.38E+00	0.097	4.68E-07	-6.33E+00
12.34	0.058	1.14E-06	-5.94E+00	0.400	6.12E-06	-5.21E+00	0.921	4.44E-06	-5.35E+00
12.09	0.026	5.01E-07	-6.30E+00	0.127	1.95E-06	-5.71E+00	0.109	5.28E-07	-6.28E+00
12.04	0.098	1.92E-06	-5.72E+00	0.288	4.41E-06	-5.36E+00	0.123	5.96E-07	-6.22E+00
12.02	0.079	1.56E-06	-5.81E+00	0.285	4.36E-06	-5.36E+00	0.113	5.45E-07	-6.26E+00
11.98	2.352	4.62E-05	-4.34E+00	0.302	4.62E-06	-5.34E+00	0.065	3.15E-07	-6.50E+00
11.97	0.086	1.68E-06	-5.77E+00	0.109	1.67E-06	-5.78E+00	0.085	4.11E-07	-6.39E+00
11.95	1.482	2.91E-05	-4.54E+00	1.125	1.72E-05	-4.76E+00	0.095	4.57E-07	-6.34E+00
11.91	0.115	2.26E-06	-5.65E+00	0.536	8.20E-06	-5.09E+00	0.098	4.73E-07	-6.33E+00
11.9	0.089	1.75E-06	-5.76E+00	0.230	3.52E-06	-5.45E+00	0.097	4.70E-07	-6.33E+00
11.88	2.388	4.69E-05	-4.33E+00	0.158	2.42E-06	-5.62E+00	0.146	7.06E-07	-6.15E+00
11.85	0.102	2.00E-06	-5.70E+00	0.119	1.81E-06	-5.74E+00	0.097	4.69E-07	-6.33E+00
11.81	0.528	1.04E-05	-4.98E+00	0.145	2.22E-06	-5.65E+00	0.077	3.73E-07	-6.43E+00
11.77	0.109	2.13E-06	-5.67E+00	0.194	2.97E-06	-5.53E+00	0.001	5.41E-09	-8.27E+00
11.7	0.085	1.68E-06	-5.78E+00	0.258	3.94E-06	-5.40E+00	0.056	2.68E-07	-6.57E+00
11.69	0.117	2.29E-06	-5.64E+00	0.240	3.67E-06	-5.44E+00	0.113	5.47E-07	-6.26E+00
11.63	0.128	2.51E-06	-5.60E+00	0.163	2.49E-06	-5.60E+00	0.158	7.65E-07	-6.12E+00
11.6	0.133	2.61E-06	-5.58E+00	0.076	1.17E-06	-5.93E+00	0.081	3.90E-07	-6.41E+00
11.46	0.146	2.86E-06	-5.54E+00	0.041	6.20E-07	-6.21E+00	0.016	7.77E-08	-7.11E+00
11.42	4.162	8.17E-05	-4.09E+00	0.222	3.40E-06	-5.47E+00	0.090	4.34E-07	-6.36E+00
11.32	0.159	3.13E-06	-5.50E+00	0.230	3.52E-06	-5.45E+00	0.026	1.26E-07	-6.90E+00
11.29	0.158	3.11E-06	-5.51E+00	0.328	5.01E-06	-5.30E+00	0.045	2.17E-07	-6.66E+00
11.27	0.158	3.10E-06	-5.51E+00	0.231	3.53E-06	-5.45E+00	0.427	2.06E-06	-5.69E+00
11.16	0.153	3.00E-06	-5.52E+00	0.163	2.49E-06	-5.60E+00	0.079	3.80E-07	-6.42E+00
11.09	0.158	3.11E-06	-5.51E+00	0.134	2.05E-06	-5.69E+00	0.064	3.10E-07	-6.51E+00
11.05	2.172	4.26E-05	-4.37E+00	0.540	8.26E-06	-5.08E+00	0.073	3.51E-07	-6.45E+00
11.04	0.172	3.37E-06	-5.47E+00	0.189	2.89E-06	-5.54E+00	0.095	4.60E-07	-6.34E+00
11.03	2.419	4.75E-05	-4.32E+00	0.262	4.01E-06	-5.40E+00	0.066	3.18E-07	-6.50E+00
11.01	0.194	3.81E-06	-5.42E+00	0.378	5.77E-06	-5.24E+00	0.131	6.31E-07	-6.20E+00
10.97	2.516	4.94E-05	-4.31E+00	0.555	8.49E-06	-5.07E+00	0.060	2.91E-07	-6.54E+00
10.83	0.194	3.80E-06	-5.42E+00	0.093	1.42E-06	-5.85E+00	0.073	3.54E-07	-6.45E+00
10.79	0.005	1.06E-07	-6.97E+00	1.717	2.63E-05	-4.58E+00	0.038	1.85E-07	-6.73E+00
10.75	0.202	3.97E-06	-5.40E+00	1.602	2.45E-05	-4.61E+00	0.073	3.54E-07	-6.45E+00
10.72	0.226	4.43E-06	-5.35E+00	0.108	1.65E-06	-5.78E+00	0.077	3.71E-07	-6.43E+00
10.61	0.217	4.26E-06	-5.37E+00	0.151	2.31E-06	-5.64E+00	0.098	4.72E-07	-6.33E+00
10.59	2.723	5.35E-05	-4.27E+00	0.457	6.98E-06	-5.16E+00	0.062	3.00E-07	-6.52E+00
10.52	0.101	1.99E-06	-5.70E+00	0.256	3.91E-06	-5.41E+00	0.136	6.58E-07	-6.18E+00
10.34	0.129	2.53E-06	-5.60E+00	0.269	4.12E-06	-5.39E+00	0.046	2.23E-07	-6.65E+00
10.31	0.104	2.05E-06	-5.69E+00	0.282	4.31E-06	-5.37E+00	0.059	2.83E-07	-6.55E+00
10.21	0.213	4.18E-06	-5.38E+00	0.329	5.03E-06	-5.30E+00	0.029	1.42E-07	-6.85E+00
10.08	0.198	3.89E-06	-5.41E+00	0.030	4.63E-07	-6.33E+00	0.054	2.60E-07	-6.59E+00
10.03	0.121	2.37E-06	-5.63E+00	0.218	3.33E-06	-5.48E+00	0.070	3.37E-07	-6.47E+00
9.45	0.259	5.09E-06	-5.29E+00	0.412	6.30E-06	-5.20E+00	0.054	2.62E-07	-6.58E+00
9.33	0.473	9.28E-06	-5.03E+00	0.036	5.46E-07	-6.26E+00	0.050	2.42E-07	-6.62E+00
9.11	0.205	4.01E-06	-5.40E+00	0.442	6.75E-06	-5.17E+00	0.084	4.06E-07	-6.39E+00
9	0.133	2.61E-06	-5.58E+00	0.029	4.44E-07	-6.35E+00	0.036	1.71E-07	-6.77E+00
8.72	4.632	9.09E-05	-4.04E+00	0.031	4.68E-07	-6.33E+00	0.103	4.97E-07	-6.30E+00
8.48	0.285	5.59E-06	-5.25E+00	0.209	3.20E-06	-5.50E+00	0.019	9.39E-08	-7.03E+00
7.12	0.467	9.17E-06	-5.04E+00	0.028	4.22E-07	-6.37E+00	0.031	1.51E-07	-6.82E+00
7.06	0.339	6.65E-06	-5.18E+00	0.203	3.11E-06	-5.51E+00	0.098	4.72E-07	-6.33E+00
6.4	0.184	3.61E-06	-5.44E+00	0.378	5.78E-06	-5.24E+00	0.102	4.90E-07	-6.31E+00
5.82	0.222	4.36E-06	-5.36E+00	1.284	1.96E-05	-4.71E+00	0.100	4.80E-07	-6.32E+00
1.12	0.542	1.06E-05	-4.97E+00	1.959	3.00E-05	-4.52E+00	0.294	1.42E-06	-5.85E+00

APPENDIX F

ML results

Table F-1 the ANC results of cement company sample

	Day	Ti	Al	Accumulate	Ba	Accumulate	Ca	Accumulate	Cd	Accumulate
Sccc	0.25	0.655	1.747	1.747	0.240	0.240	208.822	208.822	0.005	0.005
Sccc	1.00	1.457	2.378	4.125	0.260	0.500	211.328	420.150	0.005	0.009
Sccc	2.25	2.727	3.077	7.202	0.326	0.826	223.666	643.816	0.005	0.014
Sccc	4.00	4.486	3.521	10.723	0.337	1.163	221.834	865.650	0.004	0.018
Sccc	9.00	9.493	5.139	15.863	0.582	1.744	246.606	1112.256	0.006	0.024
Sccc	16.00	16.496	5.597	21.459	0.448	2.193	214.818	1327.074	0.004	0.028
Sccc	36.00	36.498	7.579	29.038	0.632	2.824	245.074	1572.148	0.004	0.033
Sccc	64.00	64.499	4.946	33.984	0.348	3.172	226.756	1798.904	0.005	0.037
	Day	Ti	Cr	Accumulate	Cu	Accumulate	Fe	Accumulate	K	Accumulate
Sccc	0.25	0.655	0.048	0.048	0.108	0.108	0.108	0.108	105.160	105.160
Sccc	1.00	1.457	0.022	0.070	0.022	0.130	0.058	0.166	65.715	170.875
Sccc	2.25	2.727	0.021	0.091	0.021	0.151	0.046	0.211	69.857	240.732
Sccc	4.00	4.486	0.020	0.111	0.017	0.168	0.038	0.250	63.080	303.812
Sccc	9.00	9.493	0.024	0.135	0.025	0.193	0.030	0.280	94.824	398.636
Sccc	16.00	16.496	0.020	0.155	0.046	0.238	0.034	0.314	73.483	472.119
Sccc	36.00	36.498	0.016	0.171	0.022	0.260	0.036	0.350	92.664	564.783
Sccc	64.00	64.499	0.023	0.194	0.022	0.282	0.040	0.390	31.695	596.478
	Day	Ti	Li	Accumulate	Mg	Accumulate	Mn	Accumulate	Na	Accumulate
Sccc	0.25	0.655	0.042	0.042	0.107	0.107	0.006	0.006	17.014	17.014
Sccc	1.00	1.457	0.037	0.079	0.101	0.208	0.004	0.010	9.277	26.291
Sccc	2.25	2.727	0.041	0.120	0.101	0.309	0.004	0.013	10.153	36.444
Sccc	4.00	4.486	0.040	0.160	0.105	0.414	0.004	0.017	9.246	45.690
Sccc	9.00	9.493	0.065	0.225	0.087	0.500	0.004	0.021	15.917	61.607
Sccc	16.00	16.496	0.062	0.287	0.104	0.605	0.005	0.026	12.767	74.374
Sccc	36.00	36.498	0.096	0.383	0.077	0.681	0.004	0.030	18.131	92.505
Sccc	64.00	64.499	0.100	0.483	0.092	0.773	0.003	0.033	7.436	99.941
	Day	Ti	NI	Accumulate	Pb	Accumulate	V	Accumulate	Zn	Accumulate
Sccc	0.25	0.655	0.040	0.040	0.107	0.107	0.006	0.006	0.078	0.078
Sccc	1.00	1.457	0.035	0.075	0.103	0.210	0.004	0.010	0.044	0.122
Sccc	2.25	2.727	0.031	0.106	0.106	0.316	0.004	0.014	0.047	0.169
Sccc	4.00	4.486	0.033	0.139	0.102	0.418	0.004	0.018	0.047	0.215
Sccc	9.00	9.493	0.033	0.173	0.111	0.530	0.002	0.020	0.049	0.264
Sccc	16.00	16.496	0.035	0.208	0.108	0.638	0.006	0.026	0.028	0.292
Sccc	36.00	36.498	0.031	0.239	0.111	0.749	0.004	0.030	0.047	0.339
Sccc	64.00	64.499	0.032	0.271	0.108	0.857	0.006	0.036	0.050	0.389

Table F-2 the ANC results of M0 sample

M0	Day	Ti	Al	Accumulate	Ba	Accumulate	Ca	Accumulate	Cd	Accumulate
0%	0.25	0.655	1.333	1.333	0.193	0.193	201.970	201.970	0.005	0.005
0%	1.00	1.457	2.793	4.127	0.254	0.447	212.740	414.710	0.006	0.011
0%	2.25	2.727	3.350	7.476	0.252	0.699	233.340	648.050	0.005	0.015
0%	4.00	4.486	3.867	11.343	0.239	0.937	233.870	881.920	0.005	0.020
0%	9.00	9.493	5.032	16.375	0.401	1.338	261.530	1143.450	0.005	0.025
0%	16.00	16.496	4.887	21.262	0.323	1.662	251.360	1394.810	0.005	0.030
0%	36.00	36.498	6.812	28.075	0.438	2.100	257.710	1652.520	0.005	0.035
0%	64.00	64.499	5.347	33.421	0.302	2.401	236.290	1888.810	0.005	0.040
M0	Day	Ti	Cr	Accumulate	Cu	Accumulate	Fe	Accumulate	K	Accumulate
0%	0.25	0.655	0.032	0.032	0.020	0.020	0.056	0.056	33.666	33.666
0%	1.00	1.457	0.041	0.073	0.019	0.038	0.029	0.085	36.093	69.759
0%	2.25	2.727	0.037	0.111	0.020	0.058	0.039	0.124	34.625	104.384
0%	4.00	4.486	0.039	0.149	0.023	0.081	0.033	0.158	31.252	135.636
0%	9.00	9.493	0.054	0.203	0.018	0.099	0.024	0.181	46.002	181.638
0%	16.00	16.496	0.116	0.319	0.021	0.120	0.032	0.214	36.519	218.157
0%	36.00	36.498	0.037	0.356	0.022	0.142	0.031	0.245	35.616	253.773
0%	64.00	64.499	0.032	0.388	0.018	0.160	0.028	0.273	19.778	273.551
M0	Day	Ti	Li	Accumulate	Mg	Accumulate	Mn	Accumulate	Na	Accumulate
0%	0.25	0.655	0.023	0.023	0.080	0.080	0.004	0.004	12.730	0.023
0%	1.00	1.457	0.031	0.054	0.068	0.147	0.003	0.007	13.910	0.031
0%	2.25	2.727	0.030	0.084	0.076	0.223	0.004	0.011	12.964	0.030
0%	4.00	4.486	0.034	0.118	0.080	0.302	0.004	0.014	12.148	0.034
0%	9.00	9.493	0.058	0.176	0.059	0.362	0.003	0.018	18.920	0.058
0%	16.00	16.496	0.058	0.234	0.079	0.441	0.004	0.021	13.996	0.058
0%	36.00	36.498	0.100	0.334	0.078	0.519	0.004	0.025	12.778	0.100
0%	64.00	64.499	0.100	0.435	0.098	0.616	0.003	0.028	5.273	0.100
M0	Day	Ti	NI	Accumulate	Pb	Accumulate	V	Accumulate	Zn	Accumulate
0%	0.25	0.655	0.033	0.033	0.107	0.107	0.004	0.004	0.045	0.045
0%	1.00	1.457	0.029	0.062	0.109	0.216	0.003	0.007	0.025	0.070
0%	2.25	2.727	0.030	0.092	0.109	0.325	0.003	0.010	0.026	0.096
0%	4.00	4.486	0.030	0.122	0.105	0.430	0.004	0.013	0.040	0.136
0%	9.00	9.493	0.029	0.151	0.109	0.539	0.002	0.015	0.031	0.166
0%	16.00	16.496	0.032	0.183	0.106	0.645	0.003	0.018	0.036	0.203
0%	36.00	36.498	0.032	0.215	0.108	0.753	0.003	0.021	0.041	0.244
0%	64.00	64.499	0.027	0.242	0.100	0.852	0.007	0.028	0.044	0.288

Table F-3 the ANC results of M1 sample

M1	Day	Ti	Al	Accumulate	Ba	Accumulate	Ca	Accumulate	Cd	Accumulate
1%	0.25	0.655	1.406	1.406	0.199	0.199	178.950	178.950	0.004	0.004
1%	1.00	1.457	2.236	3.642	0.202	0.402	203.830	382.780	0.004	0.009
1%	2.25	2.727	2.629	6.271	0.261	0.663	221.750	604.530	0.004	0.013
1%	4.00	4.486	3.074	9.345	0.251	0.914	218.620	823.150	0.005	0.018
1%	9.00	9.493	4.337	13.682	0.333	1.247	253.800	1076.950	0.005	0.023
1%	16.00	16.496	4.675	18.357	0.380	1.627	249.940	1326.890	0.004	0.027
1%	36.00	36.498	6.147	24.504	0.405	2.032	260.170	1587.060	0.005	0.031
1%	64.00	64.499	1.196	25.700	0.063	2.094	39.310	1626.370	0.229	0.260
M1	Day	Ti	Cr	Accumulate	Cu	Accumulate	Fe	Accumulate	K	Accumulate
1%	0.25	0.655	0.181	0.181	0.018	0.018	0.081	0.081	34.756	34.756
1%	1.00	1.457	0.194	0.375	0.022	0.041	0.045	0.126	34.009	68.765
1%	2.25	2.727	0.195	0.570	0.021	0.062	0.050	0.176	32.840	101.605
1%	4.00	4.486	0.204	0.773	0.019	0.081	0.030	0.206	31.381	132.986
1%	9.00	9.493	0.287	1.060	0.021	0.102	0.035	0.240	46.746	179.732
1%	16.00	16.496	0.267	1.327	0.023	0.126	0.032	0.272	32.548	212.280
1%	36.00	36.498	0.262	1.590	0.022	0.147	0.037	0.309	36.629	248.909
1%	64.00	64.499	0.051	1.641	0.003	0.150	0.004	0.313	9.164	258.073
M1	Day	Ti	Li	Accumulate	Mg	Accumulate	Mn	Accumulate	Na	Accumulate
1%	0.25	0.655	0.015	0.015	0.100	0.100	0.005	0.005	12.556	12.556
1%	1.00	1.457	0.019	0.034	0.094	0.194	0.004	0.008	12.058	24.614
1%	2.25	2.727	0.020	0.054	0.090	0.283	0.004	0.013	11.710	36.324
1%	4.00	4.486	0.021	0.075	0.091	0.375	0.003	0.016	11.015	47.339
1%	9.00	9.493	0.039	0.114	0.102	0.476	0.012	0.028	18.193	65.532
1%	16.00	16.496	0.041	0.155	0.084	0.560	0.004	0.032	12.295	77.827
1%	36.00	36.498	0.069	0.225	0.085	0.645	0.004	0.036	12.644	90.471
1%	64.00	64.499	0.005	0.229	0.035	0.680	0.001	0.037	2.262	92.733
M1	Day	Ti	NI	Accumulate	Pb	Accumulate	V	Accumulate	Zn	Accumulate
1%	0.25	0.655	0.032	0.032	0.098	0.098	0.005	0.005	0.041	0.041
1%	1.00	1.457	0.036	0.067	0.110	0.208	0.005	0.009	0.032	0.073
1%	2.25	2.727	0.036	0.103	0.101	0.309	0.002	0.011	0.034	0.107
1%	4.00	4.486	0.028	0.131	0.110	0.419	0.004	0.015	0.024	0.131
1%	9.00	9.493	0.031	0.162	0.103	0.522	0.002	0.017	0.043	0.174
1%	16.00	16.496	0.031	0.193	0.111	0.633	0.002	0.020	0.039	0.213
1%	36.00	36.498	0.034	0.227	0.107	0.741	0.001	0.020	0.044	0.258
1%	64.00	64.499	0.009	0.236	0.035	0.776	0.059	0.079	0.010	0.268

Table F-4 the ANC results of M2 sample

M2	Day	Ti	Al	Accumulate	Ba	Accumulate	Ca	Accumulate	Cd	Accumulate
2%	0.25	0.655	1.259	1.259	0.158	0.158	175.390	175.390	0.005	0.005
2%	1.00	1.457	1.961	3.220	0.219	0.377	204.360	379.750	0.005	0.010
2%	2.25	2.727	2.637	5.856	0.220	0.596	219.920	599.670	0.004	0.014
2%	4.00	4.486	3.580	9.436	0.312	0.909	239.750	839.420	0.003	0.017
2%	9.00	9.493	4.679	14.114	0.427	1.335	264.460	1103.880	0.005	0.022
2%	16.00	16.496	4.634	18.749	0.341	1.676	250.710	1354.590	0.004	0.026
2%	36.00	36.498	4.713	23.461	0.360	2.036	257.970	1612.560	0.005	0.030
2%	64.00	64.499	1.250	24.711	0.055	2.091	38.658	1651.218	0.231	0.261
M2	Day	Ti	Cr	Accumulate	Cu	Accumulate	Fe	Accumulate	K	Accumulate
2%	0.25	0.655	0.357	0.357	0.019	0.019	0.078	0.078	38.211	38.211
2%	1.00	1.457	0.354	0.711	0.021	0.040	0.067	0.145	34.106	72.317
2%	2.25	2.727	0.412	1.122	0.021	0.061	0.066	0.211	42.285	114.602
2%	4.00	4.486	0.372	1.494	0.019	0.080	0.067	0.277	38.830	153.432
2%	9.00	9.493	0.720	2.214	0.021	0.101	0.039	0.316	59.260	212.692
2%	16.00	16.496	0.580	2.794	0.022	0.122	0.041	0.357	29.237	241.929
2%	36.00	36.498	0.534	3.328	0.022	0.144	0.039	0.396	30.693	272.622
2%	64.00	64.499	0.108	3.436	0.003	0.148	0.003	0.400	8.928	281.550
M2	Day	Ti	Li	Accumulate	Mg	Accumulate	Mn	Accumulate	Na	Accumulate
2%	0.25	0.655	0.017	0.017	0.094	0.094	0.004	0.004	12.055	12.055
2%	1.00	1.457	0.019	0.036	0.091	0.184	0.004	0.008	10.242	22.297
2%	2.25	2.727	0.023	0.060	0.097	0.281	0.004	0.012	12.568	34.865
2%	4.00	4.486	0.034	0.094	0.100	0.381	0.004	0.016	13.126	47.991
2%	9.00	9.493	0.051	0.144	0.065	0.446	0.004	0.020	21.015	69.006
2%	16.00	16.496	0.046	0.191	0.080	0.526	0.004	0.024	9.735	78.741
2%	36.00	36.498	0.067	0.258	0.081	0.607	0.004	0.028	9.399	88.140
2%	64.00	64.499	0.006	0.264	0.031	0.638	0.001	0.029	2.074	90.214
M2	Day	Ti	NI	Accumulate	Pb	Accumulate	V	Accumulate	Zn	Accumulate
2%	0.25	0.655	0.031	0.031	0.104	0.104	0.003	0.003	0.043	0.043
2%	1.00	1.457	0.031	0.062	0.102	0.206	0.003	0.007	0.039	0.082
2%	2.25	2.727	0.032	0.094	0.103	0.309	0.004	0.011	0.038	0.119
2%	4.00	4.486	0.031	0.125	0.100	0.409	0.002	0.013	0.037	0.156
2%	9.00	9.493	0.031	0.157	0.113	0.522	0.002	0.014	0.035	0.191
2%	16.00	16.496	0.035	0.191	0.099	0.621	0.003	0.017	0.032	0.223
2%	36.00	36.498	0.036	0.227	0.111	0.732	0.001	0.018	0.045	0.267
2%	64.00	64.499	0.009	0.236	0.032	0.764	0.051	0.069	0.008	0.275

APPENDIX G

NEN 7375:2004

EA NEN 7375:2004

LEACHING CHARACTERISTICS OF MOULDED OR MONOLITHIC BUILDING AND WASTE MATERIALS

DETERMINATION OF LEACHING OF INORGANIC COMPONENTS WITH THE DIFFUSION TEST

‘THE TANK TEST’

Based on a translation of the

NETHERLANDS NORMALISATION INSTITUTE STANDARD

Version 1.0

April 2005

Foreword

This standard is for use with the Environment Agency's guidance on sampling and testing of wastes to determine acceptance at landfill[1]. It relates to the determination of the leaching of inorganic components from moulded or monolithic materials using the diffusion test. It is often referred to as the tank test.

The Environment Agency has issued a separate standard for the determination of the maximum potential for leaching of inorganic components from granular waste materials.

The purpose of this diffusion test is to determine the leaching of inorganic components from moulded and monolithic materials under aerobic conditions. Other parameters that can be deduced from the test include the extent of surface rinsing and the effective diffusion coefficient that can be used to estimate the leaching over longer periods.

The diffusion test is not suitable for materials that are soluble during the timescale of the test. Criteria are set out for this.

This standard is based on a translation of the Dutch leaching characterisation standard NEN 7375 (2004)[2]. An earlier diffusion test for building materials and wastes was developed in 1995 as NEN 7345[3]. The most important differences between NEN 7375 and NEN 7345 are summarised in Annex B. European standards for the characterisation of wastes are being developed under the auspices of CEN Technical Committee 292[4], and this standard will be superseded in time by one or more of the CEN/TC 292-derived standards.

Acknowledgements

The Environment Agency is very grateful to Anton van Santen for the translation of this standard from Dutch. It would also like to acknowledge the considerable technical advice received from Dr Kathy Lewin and her colleagues at WRc plc and assistance from David Hall and his colleagues at Golder Associates (UK) Ltd.

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[1] See also Guidance on Sampling and Testing of Wastes to meet Landfill Waste Acceptance Procedures, 2005.

[2] Leaching characteristics – Determination of the leaching of inorganic components from moulded or monolithic materials with the diffusion test – Solid earthy and stony materials.

[3] NEN 7345: 1995 Leaching characteristics of solid earthy and stony building and waste materials. Determination of the availability of inorganic components for leaching.

[4] Comité Europeén de Normalisation (European Standards Organisation).

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Annex D - Assessment of a Diffusion Coefficient and Calculation of Derived Values.
Annex E - Graphical representation of diffusion controlled leaching in special cases.
Annex F - Explanation of the calculation of the upper limit for leaching in special cases.

1. Scope

This document provides a test for the determination of the leaching of inorganic components from moulded or monolithic materials using the diffusion test (the tank test).

A list of materials for which the applicability of the method has been tested, and for which the precision in terms of repeatability and reproducibility has been determined, is given in Annex A.

2. Related standards

Reference is made to the following standards (and, in brackets, UK 'Blue book' (Methods for the Examination of Waters and Associated Materials, HMSO) equivalent test methods) that should be adopted when using this interim guidance.

ISO 10523:1994	Water Quality – Determination of pH (The measurement of Electrical Conductivity and the Laboratory Determination of the pH value of Natural, Treated and Waste waters. Standing Committee of Analysts, HMSO, 1978).
ISO 7888:1985	Water Quality – Determination of electrical conductivity (The measurement of Electrical Conductivity and the Laboratory Determination of the pH value of Natural, Treated and Waste waters. Standing Committee of Analysts, HMSO, 1978).
ISO 5667-3:2003	Water Quality – Sampling – Part 3: Guidance on the preservation and handling of water samples.
BS EN 13370:2003	Characterisation of waste – Analysis of eluates – Determination of Ammonium, AOX, conductivity, Hg, phenol index, TOC, easily liberatable CN^- and F^-.
BS EN 12506:2003	Characterisation of waste – Analysis of eluates – Determination of pH, As, Ba, Cd, Cl^-, Cr VI, Cu, Mo, Ni, NO_2^-, Pb, total S, SO_4^{2-}, V and Zn.
EA NEN 7371:2004	Environment Agency standard based on a translation of the Netherlands Normalisation Institute standard - Leaching characteristics of granular building

and waste materials. The determination of the availability of inorganic components for leaching. Available from Environment Agency website.

3. Principles

The purpose of this diffusion test is to simulate the leaching of inorganic components from moulded and monolithic materials under aerobic conditions as a function of time over a period of 64 days.

The test determines the nature and properties of the material matrix under investigation by placing a complete sample in a leaching fluid (demineralised, pH neutral water) and replenishing the eluate at specified times. The concentrations of the leached components in the successive eluate fractions are measured. The pH value at which leaching takes place is determined by the material itself.

On the basis of the diffusion test results, the leached quantity per unit area can be calculated for each component analysed. Parameters can be deduced from the development of the release of components over time, including the extent of surface rinsing and the effective diffusion coefficient that can be used to estimate the leaching over longer periods.

4. Test pieces

The diffusion test requires at least one test piece, the structure, homogeneity and composition of which are representative for the material or product to be tested. The smallest dimension of this test piece (P) must be greater than 40 mm and the volume (V_p) in litres must be known.

If the material to be tested is produced in a product format of which the smallest dimension is less than 40 mm, then this product may only be used as a test piece if one side has a geometric surface area A of at least 75 cm^2.

NOTES:

1. To increase the representivity of material under test, it is acceptable to aggregate a number of pieces from a batch for the diffusion test. The volume (V_p) and the geometric surface area A is then taken as the total volume and total geometric surface area of the collective pieces.
2. If the diffusion test is being undertaken to determine the effective diffusion coefficient and/or the emission per unit mass, an extra test piece is required for an availability test. The mass (m) in kg and the density (ρ) in kg/m^3 of test piece must then be known.

5. Reagents

5.1 Demineralised Water

Demineralised water with a maximum conductivity of 1 µS/cm.

5.2 Nitric acid

Nitric acid of analytically pure quality at a concentration $c(HNO_3)$ of 1 ± 0.1 mol/l.

6. Apparatus and Equipment

The materials and equipment mentioned below must be checked before use to ensure their proper operation and absence of interferences that may affect the test results. They must not emit or absorb any of the components to be determined in the eluate.

The apparatus listed under 6.5 and 6.6 must be calibrated.

6.1 Sealable tank or bucket

Sealable tank or bucket of plastic without softening agents of volume between two and five times the volume V_p and of dimensions such that the test piece is surrounded by at least 2 cm of water on all sides.

NOTES:

1. The tank must contain a supporting construction of plastic such that the test piece is surrounded by liquid on all sides. The test piece can also be suspended on a plastic wire from the lid of the tank or bucket.
2. If the surface of the test piece is partly covered with an impervious layer, use a quantity of water (in l) between 50 and 200 times the area (in m^2) of the uncovered part of the surface of the test piece.

6.2 Filtration equipment

Filtration equipment suitable for filtration at high or low pressure which is consecutively rinsed with nitric acid (5.2) and demineralised water (5.1).

6.3 Membrane filters

Membrane filters for the filtration equipment (6.2) which have not been previously used, with a pore size of 0.45 µm.

6.4 Storage bottles

Sealable plastic storage bottles.

6.5 pH meter

pH meter calibrated in accordance with ISO 10523, with a measurement accuracy better than ± 0.05 pH units.

6.6 Conductivity meter

Conductivity meter calibrated in accordance with ISO 7888, with a readout accuracy better than ± 1%.

6.7 Measuring beaker or balance

A measuring flask with a measurement capacity of at least six times the volume V_p of the test piece and a measurement accuracy better than ± 1%, or a balance with a capacity of at least three times the weight of the test piece and a measurement accuracy better than ± 0.1%.

7. Method

The diffusion test is undertaken by successively:

- establishing the requirements for the eluate samples to be analysed in accordance with 7.1;
- determining the geometric area of the test piece intended for the diffusion test in accordance with 7.2;
- performing the diffusion test according to 7.3;
- analysing the eluate according to 7.4.

7.1 Eluate samples

Determine the quantity of eluate needed to analyse the leached components and the way in which the eluate samples must be stored through the following steps:

a) identify for what components, and by what methods, analyses are to be carried out;

b) check for each component to be analysed whether the eluate will require preservation, and the requirements for this preservation;

c) determine in the light of the above the minimum quantity of eluate necessary for each component to be analysed.

In undertaking the above, bear in mind that in order to determine whether the matrix is dissolving it may be necessary to analyse all eluate fractions for Ca, Cl and SO_4. Certainty over this is only achieved after completion of the entire test (see 7.4).

NOTE:
To prevent changes in the eluate through physical, chemical or biological reactions, the eluate samples must be preserved and stored as well as possible. Guidelines for surface water and wastewater samples have been developed in ISO 5667-3. It is recommended that these guidelines be followed for the conservation and storage of eluates.

7.2 Determination of geometric area **A** *of the test piece*

The area of the test piece is determined by measurement of the characteristic parameters of the geometric surface area.

A distinction is made between:

a) test pieces with a regular, clearly determinable geometric area;

b) test pieces with a completely or partly irregular geometric surface or test pieces that are thinner than 40 mm;

c) test pieces where no regular side can be determined.

The geometric area of test pieces in a) must be determined according to 7.2.1 if these test pieces have a minimum dimension of more than 40 mm in all directions measured perpendicular at any point on the surface.

The geometric area of test pieces in b) must be determined according to 7.2.2.

The geometric surface area of test pieces c) must be determined in accordance with 7.2.3.

NOTE:
For accurate determination of the diffusion coefficient, it is necessary to determine the geometric area of a test piece precisely and clearly. For this, test pieces or parts of test pieces must be studied for which the geometric area is easy to determine. In most situations, suitable test pieces can be found. Section 7.2.1 describes the conditions and procedure for the determination of area. The procedure for selection and determination of usable areas of test pieces is more complex for test pieces with a (partly) irregular surface. The procedures for this are given in 7.2.2 and 7.2.3 respectively. For further information, see Annex C.

7.2.1 Regular test pieces for which the entire geometric area is determined

Determination of the geometric area of a regular test piece for which the geometric area of the entire test piece can be measured clearly.

1. Divide the surface of the test piece into a number of flat or curved parts (units) such that the area of each unit can be calculated geometrically from characteristic values measured such as length, width, height and radius.
2. The units specified under 1 must be selected such that the distance between the defined geometric areas and the material is never greater than 3 mm.
3. Determine the length of the characteristic values with an accuracy of better than 1 mm.
4. Using the characteristic units measured, calculate the geometric area of each of the units selected. The geometric area A expressed in m^2 is the sum of the areas calculated for each of the units.

7.2.2 Determination of the geometric area of test pieces with a partly covered surface

Determination of the geometric area of a test piece for which:

a) the entire geometric area cannot be measured clearly;

b) one or more sides have been produced by sawing or drilling the test piece from a larger element, and where these sides should not subjected to leaching;

c) one dimension is less than 40 mm.

1. Cover the parts of the surface:
    a) for which the geometric area cannot be clearly determined, using a waterproof layer;
    b) that have been produced as sawn or drilled surfaces, using a waterproof layer;
    c) of a thin test piece (with a thickness of 40 mm or less), using a waterproof layer such that the uncovered units of the geometric area never have a mutual distance of 40 mm or less measured perpendicular at any point on the geometrically described surface.

    For covering, use a waterproof and good bonding material (for example acrylic resin or paraffin) applied to the surface of the test piece. Determine the remaining geometric area after hardening of the resin.
2. Divide the uncovered part of the surface of the test piece into a number of flat or curved parts (units) such that the area of each unit can be calculated geometrically from characteristic values measured such as length, width, height and radius.
3. The units specified under 2 must be selected such that the defined geometric areas coincide with the relevant area of the test piece, where the actual distance between the material and the defined area of the unit in the case of irregularities in the surface is never greater than 3 mm.
4. Determine the length of the characteristic values with an inaccuracy of less than 1 mm.
5. Using these, calculate the geometric area of each of the units selected. The geometric area *A* expressed in m^2 is the sum of the areas calculated for each of the units.

7.2.3 Heavily irregular test pieces with no discernible regular side

Determination of the geometric surface area of heavily irregular test pieces using the paper method.

1. Cover each surface of the test piece as tightly as possible with a piece of paper. Use for this a type of paper that has no obvious absorbent properties.
2. Fold the paper around the edges of each surface of the test piece and tear or cut the paper as accurately as possible along the folds. Also remove any pieces of paper that may protrude beyond the surface.
3. Determine the total weight of pieces of paper derived from step 2.
4. Determine the weight of sheet of paper of known area and similar properties to the paper used in step 1.
5. Determine the surface area of the test piece from the ratio of weights of paper derived in steps 3 and 4.
6. Repeat steps 1 to 5 if the diffusion test is to be based on four or more pieces aggregated together from a batch. Determine the average of the measurements obtained. This is the geometric surface area determined according to the paper method.

NOTES:

1. In the determination using the paper method, printer paper and paper for photocopiers (A4 sheets) can be used. It is important that the paper does not have any strongly water absorbent properties.

2 If the test piece is damp it may be necessary of dry the paper before weighing in step 3.

7.3 Performing the diffusion test

This diffusion test is carried out in eight stages at a temperature that may vary between 18 and 22°C.

Rinse the tank or bucket (6.1) before performance of the test with nitric acid (5.2) and then rinse with water (5.1). Then place the test piece in the tank or bucket. If more test pieces are placed in the tank (Section 4), the space between the test pieces must be a minimum of 2 cm.

7.3.1 Stage 1

Fill the tank with a quantity V determined to 1% accuracy (6.7) of water (5.1) such that:

a)OK if no part of the surface is covered:

$$2 \times V_p \leq V \leq 5 \times V_p \tag{1}$$

or

b) if parts of the surface are covered:

$$50 \times A \times f \leq V \leq 200 \times A \times f \tag{2}$$

where:

V is the volume of leaching fluid in litres;
V_p is the volume of test piece P in litres;
A is the uncovered geometric area of the test piece P in m^2;
f is a conversion factor: 1 l/m^2.

The test piece must be placed such that it is in contact with the water on all sides and the uncovered part of the test piece is submerged by at least 2 cm.

Seal the tank or bucket.

After 6 ± 0.5 h, drain off all the eluate. This is the fraction from period 1. Do not dry or rinse the test piece.

Filter over a membrane filter according to the instructions in 7.1 the quantity of eluate required for analysis (6.2 and 6.3).

For the resulting eluate, measure the pH (± 0.05) (6.5) and conductivity K_{25} (± 1 %) (6.6).

NOTES:

1. The pH value and the conductivity are required to determine if the matrix has dissolving during the test (see 8.4 and 9.3.3.)
2 The pH value gives an indication of the alkalinity of the test piece, and the change in pH during the diffusion test gives an indication of the stability of the material being investigated. Large variations in the eluate pH points towards the material not yet being in equilibrium, i.e. is not yet stabilised.

Transfer the quantity of eluate intended for analysis to the bottles of suitable size (6.4), filling each bottle with at least 10 ml.

Store the eluate samples using the procedures described in 7.1. If more than 1 ml preservative is required per 250 ml eluate, the concentrations determined in 7.4 must be corrected for this.

7.3.2 Stages 2 to 8

Immediately after drainage in stage 1 (7.3.1), fill the tank or bucket again with water (5.1). Use the same quantity V (6.7), determined to ± 1% accuracy, as used in stage 1.

Repeat the procedure described in stage 1 a further seven times as shown in Table 1 (the times apply from the immersion).

Table 1: Times at which the water must be replenished

Period (n)	Time (days)
1	0.25 ± 10%
2	1 ± 10%
3	2.25 ± 10%
4	4 ± 10%
5	9 ± 10%
6	16 ± 1
7	36 ± 1
8	64 ± 1

Determine the replenishment times (the time at which the tank has just been emptied) of each period n, to 15 minutes accuracy.

On completion of the test, weigh the solid material that may have fallen off the test piece(s) during the test and remains in the tank. This solid material must first be dried.

If during the replenishment it is found that a relatively large amount of material has fallen off the test piece(s), it is recommended not to wait until the end of the test but to remove the solid material during one or more of the replenishments, and to dry and weigh this.

Calculate the weight loss m_v (g/m^2) of material that has fallen off the test piece during the test (*g/A* (m^2) where *A* is the (uncovered) area of the test piece) in two phases:

1) the weight loss m_{va} (g/m^2) in Stages 1 to 2 of the test;

2) the weight loss m_{vb} (g/m^2) in Stages 2 to 8 of the test.

NOTE:
These two parameters give insight into the characteristics of the material. A relatively large weight loss m_{va} compared with m_{vb} indicates that the loss is a consequence of the manner in which the test piece has been made or prepared (for example, loss from an inadequately cured test piece at the start of the test, or loss as the result of manner of sawing of the test piece). A relatively large weight loss m_{vb} compared with m_{va} indicates the long term integrity of the material (for example, the ongoing loss of material indicates moderate bonding in a composite material or loss of effectiveness of the binding agent under the influence of water).

7.4 Analysis of the eluates

Analyse the eluate fractions obtained in 7.3 from periods 1 to 8.

If the measured eluates pH values and conductivities indicate dissolution of the matrix during the test, then the following calculations must be undertaken, and assessment made whether criteria 1 and 2 are satisfied. If neither criteria are satisfied, then the components Ca, SO_4 and Cl must be determined to verify whether dissolution has occurred.

1. Calculate the average value of the measured conductivities in periods 5 and 6 (S_{5-6}) in µS/cm.
2. Calculate the average value of the measured conductivities in periods 7 and 8 (S_{7-8}) in µS/cm.
3. Calculate the average pH value in periods 7 and 8 (pH_{7-8}).

Criterion 1

Check if:

$$S_{7-8} > 1.5 \times V_p/V + 10\wedge(pH_{7-8} - 11.78) + 10\wedge(2.5 - pH_{7-8})$$

where:

V is the volume of leaching fluid, in l;
V_p is the volume of the test piece, in l.

If criterion 1 is not satisfied then the matrix is not soluble, and there is no need to analyse the components Ca, Cl and SO_4.

If criterion 1 is satisfied, continue to criterion 2.

Criterion 2

Check if:

$S_{7-8} > 2 \times S_{5-6}$

If criterion 2 is not satisfied then the material is not soluble, and there is no need to analyse the components Ca, Cl and SO_4.

If criterion 2 is satisfied, then analyse Ca, Cl and SO_4 in all eluates to verify whether dissolution has occurred (see 8.3.3).

NOTES:

1. A number of standards for chemical analyses of eluate components are available. The European Standards prEN 13370:2002 and ENV 12506 are intended to define the analytical methods to be used for eluates obtained from waste characterisation tests. UK 'Blue Book' methods (Methods for the Examination of Waters and Associated Materials, HMSO) would be expected to give similar analysis results.
2 Always analyse the eluate samples within the timescales given in the guidance in ISO 5667-3.

8. Calculation

The measured leaching per eluate fraction, the cumulative leached quantities, the leaching mechanism occurring, the cumulative leaching per unit area, the surface wash-off and the upper limit of the leaching of components, for which no diffusion controlled leaching can be determined, are determined for each component under investigation by successively:

- determining the leaching per eluate fraction as per 8.1;
- determining the measured and derived cumulative leaching respectively as per 8.2;
- establishing the leaching mechanism occurring as per 8.3;
- determining the cumulative leaching per unit area as per 8.4;
- determining the surface wash-off in combination with the diffusion controlled leaching as per 8.5;
- determining the upper limit of leaching for the components for which no diffusion controlled leaching can be established, as per 8.6.

The above mentioned quantities only have relevance and may only be used if the matrix of the material does not dissolve. In 8.3.3 a check is made whether this requirements is met.

8.1 Measured leaching of a component per fraction

For each component to be studied, calculate separately the <u>measured</u> leaching per fraction using the formula:

$$E_i^* = \frac{c_i \times V}{f \times A} \qquad (3)$$

where:

E^*_i is the measured leaching of a component in fraction *i*, in mg/m^2;

c_i is the concentration of the component in fraction *i* in µg/l;
V is the volume of the eluate in l;
A is the surface area of the test piece in m^2;
f is a conversion factor: 1000 µg/mg.

The concentration c_i specified in formula (3) is the concentration originally present in the eluate; the measured value determined according to Section 7.4 must be corrected for the quantity of preservative added in Section 7.3 if this is more than 1 ml per 250 ml eluate.

If the concentration of a component in a specified eluate fraction is below the lowest limit of analytical determination, two calculations must be carried out for the component. The upper limit of E^*_i is calculated by equating c_i in formula (3) with the lowest limit of determination; the lower limit of E^*_i is calculated by setting c_i in formula (3) to 0.

8.2 Measured and derived cumulative leaching of a component

8.2.1 Measured cumulative leaching

For each component to be analysed, calculate separately the measured cumulative leaching ε^*_n in each of the periods n =1 to N, where the period n=1 lasts from the start of the test to the first replenishment time (comprises fraction i=1), period n=2 from the start of the test to the second replenishment time (comprises fractions 1 + 2), etc. Carry out this calculation as:

$$\varepsilon^*_{\mathrm{n}} = \sum_{i=1}^{n} E^*_i \qquad \text{for } n\text{=1 to } N \qquad (4)$$

where:

ε^*_n is the measured cumulative leaching of a component for period n comprising fraction i=1 to n, in mg/m^2;
E^*_i is the measured leaching of the component in fraction i in mg/m^2;
N is the number of periods equal to the number of specified replenishment times (N = 8).

The calculation method is explained as in Figure 1 below.

8.2.2 Derived cumulative leaching of a component

For each component to be analysed, calculate separately the derived cumulative leaching ε_n in each of the periods n=1 to N, where a period n lasts from the start of the test to the n^{th} replenishment time (comprises fractions i=1 to n).

Carry out this calculation as follows:

$$\varepsilon_n = (E^*_i \times \sqrt{t_i})/(\sqrt{t_i} - \sqrt{t_{i-1}}) \qquad \text{for } n\text{=1 to } N \text{ (where } i = n\text{)} \qquad (5)$$

where:

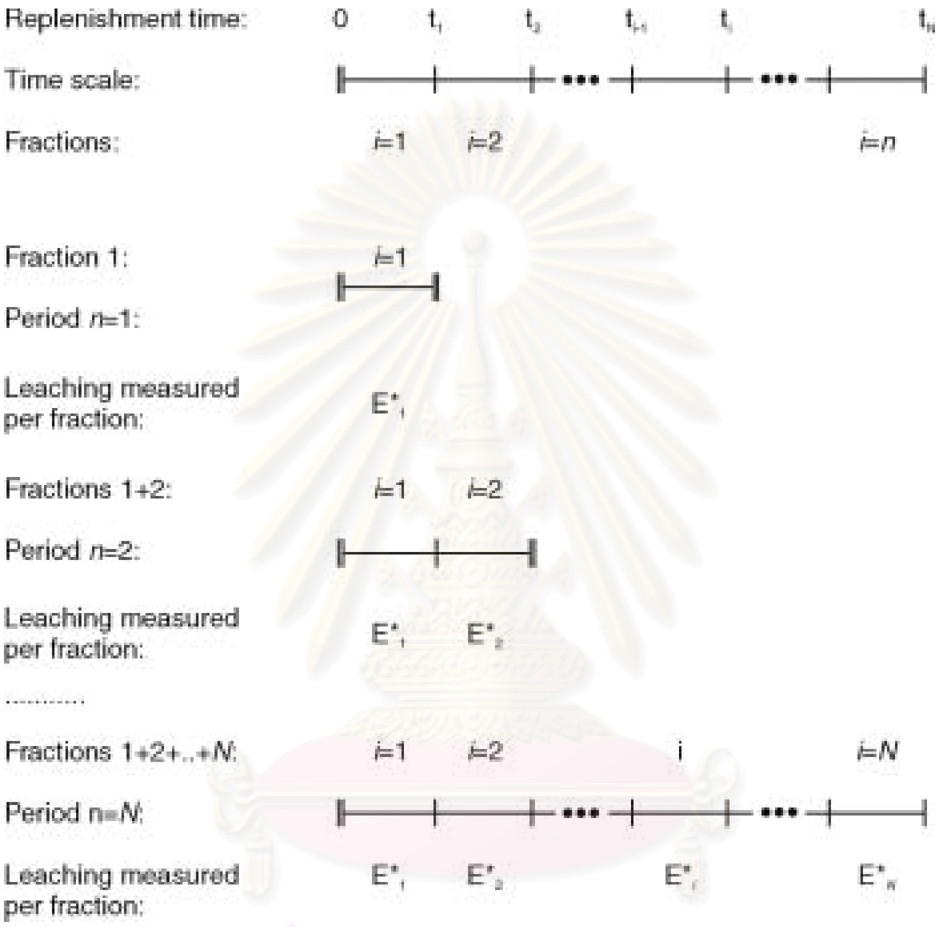
ε_n is the derived cumulative leaching of a component for period n comprising fraction i=1 to n, in mg/m^2;
E^*_i is the measured leaching of the component in fraction i, in mg/m^2;
t_i is the replenishment time of fraction i, i.e. time at end of fraction i, in s;
t_{i-1} is the replenishment time of fraction i-1, i.e. time at start of fraction i, in s.

NOTES:

1. The measured cumulative leaching ε^*_n always includes the measured leaching of previous periods. This means that any deviations in a period (for example wash-off effects) affect the following periods that can make interpretation difficult.

2 The derived cumulative leaching ε_n determines only the cumulative leaching up to and including period i on the basis of the measured leaching in period i. These values can be used to assess whether the leaching is determined by diffusion (see Section 8.3).

Figure 1: Diagrammatic overview of terms used in this standard in determining the leaching behaviour of a test piece.
The fractions $i=1$ to $i=N$ indicate the successive eluate fractions;
the period $n=x$ corresponds to the sum of the number of fractions $i=1$ to $i=x$.



8.3 *Determination of the leaching mechanism(s) occurring in the diffusion test*

Based on the leaching of components as set out in 7.4, establish whether the matrix of the test piece is dissolving during the conduct of the test. If this is not the case, then for all individual components determine whether leaching is diffusion controlled or whether other leaching mechanisms also contribute.

Carry out the procedure in this section for each of the components to be studied.

NOTE:
To support and monitor the further assessment and calculation of the leaching behaviour, it is recommended that the cumulative leaching determined in Sections 8.1 and 8.2 be shown graphically (see Annex E). For this, plot for each individual component the logarithm of the derived cumulative leaching ε_n against the logarithm of the time t_i for $n=1$ to N in order to allow a visual inspection of the measurement data. On the same graph also plot the logarithm of the measured cumulative leaching ε^*_n.

8.3.1 Definition of incremental periods

Group the eluate fractions collected in the periods 1 to 8 as follows:

Order	**Eluate fraction**	**Increment a-b**
1	Fractions 2 to 7	Increment 2-7 incl
2	Fractions 5 to 8	Increment 5-8 incl
3	Fractions 4 to 7	Increment 4-7 incl
4	Fractions 3 to 6	Increment 3-6 incl
5	Fractions 2 to 5	Increment 2-5 incl
6	Fractions 1 to 5	Increment 1-4 incl

Analyse the leachate values according to the procedure in 8.3.2, beginning with increment 2-7, followed by increment 5-8 and so on. Use this order for each component.

NOTES:

1 The method to establish whether the leaching mechanism is diffusion controlled is built up as follows:

a) Firstly, the eluate fractions obtained and analysed in periods 1 to 8 are divided into increments that are long enough to establish the leaching mechanism.

a) For all components to be determined, and for each of the divided increments in a), the concentration factor (CF), the slope (rc) of the linear regression line of log ε versus log t and the standard deviation of the slope (sd_{rc}) are determined and recorded in a table (see 8.3.2).

c) Subsequently, on the basis of these values, check that the matrix does not dissolve (see 8.3.3). If the test piece (the matrix) does dissolve, then the leaching from this test piece can not be determined with the diffusion test.

d) If the matrix does not dissolve, then for all components, per increment, a check is made whether the quantity of diffusion controlled leaching can be determined. The first increment in the order given in a) for which the quantity of diffusion controlled leaching can be determined is the "leaching mechanism determining increment".

e) Subsequently, it is determined whether, in addition to diffusion, other leaching mechanisms are involved.

f) If for certain components no diffusion controlled leaching can be established (and there is no suggestion of the matrix dissolving), then an estimate can be made of the upper limit of leaching.

2 Increment 2-7 is considered as a "total increment" for the entire diffusion test. The first fraction is not included in order to eliminate interpretative errors in the analysis due to wash-off effects. The last fraction is also not included in the total increment to eliminate as far as possible depletion of a certain component during the test.

8.3.2 Incremental analysis per component

For each component to be studied, undertake an incremental analysis as follows:

Step 1:

For each increment a-b determine the concentration factor $CF_{a\text{-}b}$:

$$CF_{a\text{-}b} = \frac{\text{mean concentration in the increment}}{\text{lowest limit of determination}} \qquad (6)$$

If in all the fractions in the increment a-b, the measured concentrations for the component under investigation are all higher than the lowest limit of determination for that component, <u>and</u> $CF_{a\text{-}b} = 1.5$, then continue to Stage 2. If this is not the case, then for this component no leaching mechanism can be determined in this particular increment.

NOTE:

If for an increment the factor $CF_{a\text{-}b}$ for the component under investigation is less than 1.5, the values measured in that increment are too low to allow determination of the leaching mechanism. Also, if in one of the fractions of the increment the concentration is lower than the lowest limit of determination, then it cannot be proved whether the leaching is diffusion controlled.

Step 2:

Using linear regression of the log ε_n - log t_i relation (with $i = n$), determine for each increment the slope rc and the associated standard deviation, sd_{rc} calculated from the regression analysis.

The concentration factors, slopes and standard deviations can be given clearly as shown in Table 2 to support and simplify the assessment and further processing of the test results.

Table 2: Overview of concentration factors, slopes and standard deviations as determined in the following increments.

Increment a-b	CF_{a-b}	rc	Sd_{rc}
Increment 2-7			
Increment 5-8			
Increment 4-7			
Increment 3-6			
Increment 2-5			
Increment 1-4			

8.3.3 Determining whether the matrix dissolves

The determination of the leaching mechanism and the quantification of the leaching per component only have meaning if the matrix of the material does not dissolve. In 7.4, two criteria are used examine whether, in principle, this could be the case.

If in 7.4 both criteria are not satisfied, then the material does not dissolve. In this case, proceed to 8.3.4.

If in 7.4 both criteria are satisfied, proceed then on the basis of the values for Ca, Cl and SO_4 determined in 8.3.2 to evaluate whether criterion 3 is satisfied.

Criterion 3:

For at least 2 of the 3 above mentioned components, check whether $CF_{5-8} > 3.0$ and $rc_{5-8} > 0.8$.

If criterion 3 is not satisfied, then the matrix does not dissolve. In this case, proceed to 8.3.4.

If criterion 3 is satisfied, then the matrix does dissolve. In this case the leaching from this test piece cannot be determined through the diffusion test.

NOTE:
This criterion will be satisfied principally by gypsum product and materials with a high salt concentration.

8.3.4 Determining whether the leaching of the different components is diffusion controlled or whether other leaching mechanisms are involved

On the basis of the concentration factors and slopes calculated in 8.3.2, it can be determined which leaching mechanism(s) are involved in the release of different components from the test piece. A precondition for this is that the standard deviation of the slope must meet certain requirements. With fully diffusion controlled leaching, the slope is exactly 0.5.

The significance of the slope of the different increments is summarised in Table 3.

Table 3: Significance of slopes of the different increments.

Increment a-b	Slope, rc		
	≤ 0.35	> 0.35 and ≤0.65	> 0.65
Increment 2-7	Surface wash-off	Diffusion	Dissolution
Increment 5-8	Depletion	Diffusion	Dissolution
Increment 4-7	Depletion	Diffusion	Dissolution
Increment 3-6	Depletion	Diffusion	Dissolution
Increment 2-5	Depletion	Diffusion	Dissolution
Increment 1-4	Surface wash-off	Diffusion	Delayed diffusion or dissolution

Step 1:

Determine per component for all increments, in the order given in Table 3 beginning with increment 2-7, if the leaching mechanism is diffusion controlled on the basis of the following criteria. The first increment for a component for which the quantity of diffusion controlled leaching can be established is deemed the “leaching mechanism determining increment” for that component.

Criteria for diffusion controlled leaching in increment *a-b*

$CF_{a\text{-}b} \geq 1.5$ $\quad$ $sd_{rc} \leq 0.5$ $\quad$ $0.35 < rc \leq 0.65$

If the above criteria are satisfied, then the diffusion controlled leaching of the component concerned can be calculated using the formulas in 8.4.

If, as well as diffusion controlled leaching, there is also an indication of surface wash-off in increment 1-4, then this surface wash-off can be quantified using the formulas in 8.5.

Step 2:

If for certain components diffusion controlled leaching cannot be established in any of the increments (and the material does not dissolve according to the criteria in 8.3.3), then for that component an upper limit for leaching is determined. For this, proceed to 8.6, in which formulas are given for various situations dependent on the controlling leaching mechanism.

NOTE:
In Annex E graphical representations are given of each extreme case of leaching. Depletion events are indicated in Figure E2, surface wash-off in Figure E4 and chemical changes in the material in Figures E3, E5 and E6.

8.4 Calculation of the diffusion controlled leaching of a component per unit surface area

The calculation of leaching of a component per unit surface area must be undertaken in all cases, where the diffusion controlled leaching has been established by the increment analysis in 8.3.4.

The derived leaching of a component per unit surface area over an arbitrary time interval can be determined by the formula:

$$\varepsilon_{x,y} = \left\{\sqrt{t_y} - \sqrt{t_x}\right\} \left\{ \prod_{i=a}^{b} \frac{E_i^*}{\sqrt{t_i} - \sqrt{t_{i-1}}} \right\}^{\frac{1}{1+b-a}} \qquad (7)$$

where:

$\varepsilon_{x,y}$ is the derived leaching of a component in the time period t_x and t_y, in m^2/s;

E^*_i	is the <u>measured</u> leaching of the component in fraction i in mg/m^2;
t_x	is the start time of the interval measured from the start of the test, in days;
t_y	is the end time of the interval measured from the start of the test, in days;
t_i	is the end time of fraction i, which is part of the increment a-b, for which diffusion has been established, measured from the start of the test, in days;
t_{i-1}	is the start time of fraction i, measured from the start of the test, in days. This is part of the increment a-b, for which diffusion has been established..
a,b	are dimensionless indices by which an increment a-b is indicated for which a diffusion mechanism is established.

NOTES:

1. The product function in (7) is a measure for the average leaching rate, taking into account the diffusion controlled nature of the leaching process. The leaching is corrected by the square root of the times. In practice, this method of calculation leads to a <u>calculated</u> average negative logarithm of the effective diffusion coefficient (pD_e). For the determination of the average effective diffusion coefficient D_e, see Annex D1.
2. If, for example, a diffusion controlled mechanism is established in increment 2-7, then the product function takes the values a=2 and b=7:

$$\left\{\prod_{i=1}^{7} U_i\right\}^{\frac{1}{6}} = \left\{U_2 \times U_3 \times U_4 \times U_5 \times U_6 \times U_7\right\}^{\frac{1}{6}} \qquad (8)$$

where:

$$U_i = \frac{E_i^*}{\sqrt{t_i} - \sqrt{t_{i-1}}}$$

Calculate for each component under investigation separately the <u>derived</u> cumulative leaching per unit are over 64 days, ε_{64}, with the formula:

$$\varepsilon_{64} = \sqrt{64}\left\{\prod_{i=a}^{b} \frac{E_i^*}{\sqrt{t_i} - \sqrt{t_{i-1}}}\right\}^{\frac{1}{1+b-a}} \qquad (9)$$

where:

ε_{64}	is the <u>derived</u> cumulative leaching for a component over 64 days, in mg/m^2;
E^*_i	is the <u>measured</u> leaching of the component in fraction i in mg/m^2;
t_i	is the end time of fraction i for which diffusion has been established, measured from the start of the test, in days;
t_{i-1}	is the start time of fraction i for which diffusion has been established, measured from the start of the test, in days;
a,b	are dimensionless indices by which an increment a-b is indicated for which a diffusion mechanism is established.

Calculate also for each component under investigation separately the <u>measured</u> cumulative leaching per unit surface area over 64 days ε^*_{64} using the formula:

$$\varepsilon^*_{64} = \sum_{i=1}^{N} E_i^* \qquad (10)$$

where:

ε^*_{64}	is the <u>measured</u> cumulative leaching for a component per unit surface area over 64 days, in mg/m^2;
E^*_i	is the <u>measured</u> leaching of the component in fraction i, in mg/m^2;

N is the number of periods, equal to the number of prescribed refreshing intervals (N=8).

If the measured cumulative leaching over 64 days (ε^*_{64}), calculated using formula (10) is smaller that the derived cumulative leaching calculated using formula (9) and also the slope of increments 3-6 and 4-7 are both smaller than 0.35, then the measured cumulative emission over 64 days is considered to be the upper limit of leaching.

8.5 Quantifying the surface wash-off in combination with diffusion-controlled leaching

The surface wash-off of a component per unit surface area can only be determined where the incremental analysis in 8.3.4 has established that the leaching of that component is diffusion controlled.

If surface wash-off is indicated in the first two factions of increment 1-4 (rc $\leq$ 0.35) whilst in one or more of the following increments diffusion controlled loss is accepted, then the amount of surface wash-off ($\varepsilon_{wash,1\text{-}2}$) in mg/m^2 is given by:

$$\varepsilon_{wash,1-2} = E_1^* + E_2^* - \varepsilon_{64} \times \sqrt{1/64} \qquad (11)$$

where:

$\varepsilon_{wash,1\text{-}2}$	is the washed-off quantity of the particular component, in mg/m^2;
E^*_1	is the measured leaching of that component in fraction 1 (1/4 day), in mg/m^2;
E^*_2	is the measured leaching of that component in fraction 2 (1 day), in mg/m^2;
ε_{64}	is the calculated leached quantity of the particular component over 64 days, in mg/m^2 calculated from formula (9).

NOTE:
See Annex E, figure E4 for a graphical representation of this type of leaching.

8.6 Determination of the upper limit for leaching of components for which no diffusion can be established

The calculation of the upper limit for leaching of a component per unit surface area can only be undertaken when, according to 8.3.4, leaching of the particular component is not diffusion controlled and, according to 8.3.3, the matrix does not dissolve.

NOTE:
If the matrix does not dissolve, then for certain components for which diffusion cannot be established by the increment analysis, an estimate can still be made of the long term leaching by applying the formulas for diffusion controlled leaching.

The calculations must be considered in the order set out in the following paragraphs.

8.6.1 The concentration factor $CF_{1\text{-}8}$ is less than 1.5

If the concentration factor $CF_{1\text{-}8}$ is less than 1.5, then the upper limit of the cumulative emission over 64 days is calculated as follows:

$$\varepsilon_{64} = \varepsilon^*_{1\text{-}8} \qquad (12)$$

where $\varepsilon^*_{1\text{-}8}$ is calculated from 8.1 and 8.2.1, where c_i in Formula (3) is set equal to the lowest limit of determination.

NOTE:
If the concentration factor $CF_{1\text{-}8}$ is less than 1.5 then the average concentration for the "total increment" is less than 1.5 times the lowest limit of determination.

The upper limit for leaching over a period T from the beginning of the leaching is calculated from:

$$\varepsilon_T = \varepsilon^*_{1-8} \times \sqrt{T/64} \qquad (13)$$

where:

ε_T is the upper limit of the leaching of a component over a period T, in mg/m^2;
T is the duration of the period, in days.

8.6.2 Surface wash-off followed by low concentrations in the subsequent fractions

If through the increment analysis in 8.3.4 it is found that surface washing has occurred, followed by low concentrations on the subsequent fractions, then the upper limit for diffusion over a time period T from the start of leaching is calculated from:

$$\varepsilon_T = \varepsilon^*_{1-2} + \varepsilon^*_{3-8} \times \frac{\sqrt{T} - \sqrt{1}}{\sqrt{64} - \sqrt{1}} \qquad (14)$$

where:

ε_T is the upper limit of the leaching of a component over a period T, in mg/m^2;
$\varepsilon^*_{1\text{-}2}$ is the <u>measured</u> cumulative leaching over the increment 1-2, in mg/m^2;
$\varepsilon^*_{3\text{-}8}$ is the <u>measured</u> cumulative leaching over the increment 3-8 (upper limit, see 8.1), in mg/m^2;
T is the duration of the period, in days.

NOTE:

Formula (14) for the wash-off applies if in increment 1-4 the slope is less than 0.35 and additionally that the concentrations are well measurable, whilst the concentrations in increment 5-8 are not so measurable. Extrapolation of the measured leaching according to a diffusion controlled leaching will overestimate the true leaching. It is also not correct to extrapolate the initial wash-off using the formula for diffusion controlled leaching; in stead the wash-off should be added to the diffusion controlled leaching.

8.6.3 Possible depletion/changing chemical form

If the increment analysis in 8.3.4 reveals that for a component that in at least two of the increments 2-5 and/or 3-6 and/or 4-7 and/or 5-8 the slope is less than 0.35 and the concentration factor is greater than 1.5, then this indicates that depletion of this component may have occurred.

NOTE:

1. There are also indications of depletion if, after initial wash-off, significant concentrations are measured in the extracts in following the periods (as opposed to the situation described in 8.6.2). Extrapolation of the cumulative measured leaching will then overestimate the actual leaching. It is, however, not correct to include the initial wash-off in the formula for the diffusion controlled leaching.
2. Inert components are distinguishable by having the lowest pD_e values in the matrix under consideration, whilst the remaining components always have a higher pD_e value. This means that depletion always occurs earlier with inert components than with the other components. The appearance of an rc<0.35 in such a case can be explained by the fact that chemical conditions change, as a result of which a step change occurs to, for example, a different diffusion level, or that a mobile chemical form becomes depleted whilst a different leachable form of that component remains (more strongly) bonded in the matrix.

The upper limit for leaching over a period T from the start of leaching can then be calculated by the formula:

$$\varepsilon_T = \varepsilon^*_{1-2} + \varepsilon^*_{3-8} \times \frac{\sqrt{T} - \sqrt{1}}{\sqrt{64} - \sqrt{1}} \qquad (15)$$

where:

ε_T is the upper limit of the leaching of a component over a period T, in mg/m^2;
$\varepsilon^*_{1\text{-}2}$ is the <u>measured</u> cumulative leaching over the increment 1-2, in mg/m^2;
$\varepsilon^*_{3\text{-}8}$ is the <u>measured</u> cumulative leaching over the increment 3-8 (upper limit, see 8.1), in mg/m^2;
T is the duration of the period, in days.

8.6.4 Dissolution

If the slope for the a particular component for the total increment (2-7) is greater than 0.65 (see 8.3.4 Step 1), the leaching over 64 days is calculated as:

$$\varepsilon_{64} = \varepsilon^{*}_{1\text{-}8} \qquad (16)$$

$\varepsilon^{*}_{1\text{-}8}$ is determined as set out in 8.1 and 8.2.1, where c_i in formula (3) in 8.1 is given the value of the lowest limit of determination if the concentration of a component in a fraction is lower than the lowest limit of determination.

The upper limit of leaching over a period T from the start of leaching is then:

$$\varepsilon_T = 2 \times \varepsilon^{*}_{1-8} \times \sqrt{T/64} \qquad (17)$$

NOTE:

If the slope is greater than 0.65 then there is a possibility of dissolution of the component. This appears contrary to the finding that the test piece is not dissolving. This, however, need not be the case. It can be concluded that, viewed from the leaching mechanism of the matrix, the dissolution of the particular component has no permanent character. It is even possible that dissolution is only occurring from the outer layer of the test piece. The slope can also be greater than 0.65 if at low concentrations the influence of other components is relatively large.

8.6.5 Large spread in measured concentrations

No determination of the slope is possible in 8.3.4 step 1 where the measured concentrations exhibit a wide spread ($sd_{rc}>0.5$). In this case the leaching over 64 days is calculated by the formula:

$$\varepsilon_{64} = \varepsilon^{*}_{1\text{-}8} \qquad (18)$$

$\varepsilon^{*}_{1\text{-}8}$ is determined as set out in 8.1 and 8.2.1, where c_i in formula (3) in 8.1 is given the value of the lowest limit of determination if the concentration of a component in a fraction is lower than the lowest limit of determination.

The upper limit of leaching over a period T from the start of leaching is then:

$$\varepsilon_T = 5 \times \varepsilon^{*}_{1-8} \times \sqrt{T/64} \qquad (19)$$

where:

ε_T is the upper limit of the leaching of a component over a period T, in mg/m^2;
$\varepsilon^{*}_{1\text{-}8}$ is the measured cumulative leaching over the total duration of the test, in mg/m^2;
T is the duration of the period, in days.

NOTE:

Research has been conducted to investigate how large the error in the value of pD_e could be when $sd_{rc}>0.5$. In that case the slope rc could rise to 1.5 so that the value of pD_e would be a whole 1 log (m^2/s) lower. This is equivalent to a 10 fold overestimate of the diffusion coefficient, which means at least a three fold overestimate of the leaching. Because the value of pD_e within the period of the diffusion test can decrease even further due to changes in the chemical conditions (for example, through the leaching of lead from a reducing material), a factor of 5 is introduced in the formula for ε_T to give the assumed upper limit.

Table 4: Calculation of the upper limit of leaching of a component in special circumstances

Description	Criteria[a]	Formula for calculating ε_T
1) Measured, average concentration in all fractions is	$CF_{1\text{-}8}<1.5$	$\varepsilon_T = \varepsilon^{*}_{1-8} \times \sqrt{T/64}$ (13)

	low			
2)	Wash-off in the first two steps, after which measured concentrations are low	CF ≥ 1.5 and rc < 0.35 for increment 1-4, and CF < 1.5 for increment 5-8	$\varepsilon_T = \varepsilon^*_{1-2} + \varepsilon^*_{3-8} \times \frac{\sqrt{T} - \sqrt{1}}{\sqrt{64} - \sqrt{1}}$	(14)
3)	Possible depletion of different chemical forms	rc < 0.35 and CF ≥ 1.5 for at least two of the increments 2-5 and/or 3-6 and/or 4-7 and/or 5-8	$\varepsilon_T = \varepsilon^*_{1-2} + \varepsilon^*_{3-8} \times \frac{\sqrt{T} - \sqrt{1}}{\sqrt{64} - \sqrt{1}}$	(15)
4)	Dissolution during increment 2-7	rc > 0.65 for increment 2-7	$\varepsilon_T = 2 \times \varepsilon^*_{1-8} \times \sqrt{T/64}$	(17)
5)	Large spread in all increments	sd_{rc} > 0.5 for increments 3-6, 4-7 and 5-8	$\varepsilon_T = 5 \times \varepsilon^*_{1-8} \times \sqrt{T/64}$	(19)

[a] The parameters have the following meanings:

CF_{a-b} is the concentration factor in increment a-b

rc is the slope of the relevant increment

sd_{rc} is the standard deviation of the slope of the relevant increment

ε_T is the upper limit of leaching of a component over period T, in mg/m^2

ε^*_{a-b} is the measured cumulative leaching over the relevant increment a-b, in mg/m^2

T is the duration of the period, in days

8.6.6 Summary of situations in which the upper limit of leaching can be determined

Table 4 provides a summary of the formulas used to calculate the upper limit of leaching where there is no possibility of diffusion and the matrix is not dissolving. Further information on the exceptional cases in Table 4 are given in Annex F.

9. Report

The report must contain the following data at least:

- a reference to this standard, indicating: “in accordance Environment Agency standard EA NEN 7375:2004";
- the data necessary for identification of the test piece(s);
- source and specifications of the test piece(s);
- the nature of the material studied;
- the temperature range within which the leaching test was performed;
- the pH of the eluates collected, rounded to 0.0.5 pH-unit;
- the conductivity of the eluates collected rounded to maximum 1 significant figure;
- the components analysed and the lowest limits of determination of the components in the eluate;
- the means by which the eluates have been preserved and stored until the time of analysis;
- all concentrations measured, rounded to maximum 2 significant figures;
- the quantity of preservative added in Section 7.3 if this is more than 1 ml per 250 ml eluate;
- the amount of material fallen off the test piece(s) during the test;
- the slopes and corresponding standard deviations of all increments;
- the start and end points of the leaching mechanism-determining increment, if the leaching of the relevant component is diffusion controlled;
- the quantity of the components tested available for leaching;
- the results of the investigation into the (non-) dissolution of the test piece(s);
- the <u>calculated</u> cumulative leaching of the components tested over 64 days (ε_{64}), in mg per m^2;
- the <u>measured</u> cumulative leaching of the components tested over 64 days (ε^*_{64}), in mg per m^2;
- the evaluated possible surface wash-off of the components tested, in mg/m^2;

- the calculated upper limit in possible special circumstances of leaching of one or more components, in mg/m^2;
- the eventual weight loss during the test, in mg/m^2;
- the duration of the investigation.

If the diffusion test is not carried out fully in accordance with this standard, <u>all</u> deviations from the prescribed procedures must be indicated in the report, giving the reasons.

Annex A

Validation of the Diffusion Test

In developing the Dutch Standard, NEN 7375, a round-robin test was undertaken with 10 laboratories on 3 types of material to establish the precision of the diffusion test in terms of repeatability and reproducibility. The following is taken from the discussion presented in NEN 7375.

The error in the end result of a leaching test is composed of contributions from:

- The origin of the material (variations in the production process);
- The method of sample taking (differences in representativeness);
- The sample pre-treatment (variations in the preparation of the test piece for the leaching test);
- The leaching test itself;
- The chemical analysis (error in the determination of concentration in the eluates);

To establish the precision of the diffusion test, the contribution of these sources of error were minimized through the experimental design. Therefore, in the validation study the following starting points were used.

- Components that can be very inhomogeneous in certain materials were not included in determining the precision.
- The samples were all taken from one batch and the sample preparation was performed in one session.
- All chemical analyses were carried out by one laboratory.
- The precision was only determined for components for which the error in the chemical analysis was sufficiently small (relative standard deviation in repeatablility nominal less than 5%). For larger errors in the concentration measurement the precision of the analysis would dominate the precision of the leaching test result too much.

The test pieces examined relate to three different types of moulded materials. The table below gives an overview of the materials used and the components tested:

Table A.1: Investigated materials and components

GRAIN SIZE CLASS	MATERIAL TESTED	COMPONENTS TESTED[1)]
Moulded	Fly ash/cement mix	Na, Ba, Mo, SO_4, V
Moulded	Sand lime brick with coal dust fly ash	Na, As, (Ni), Se*, SO_4, (V)
Moulded	Building brick	Na*, As, V

1) All elements in brackets and marked * in Table A.1 were measured but not included in determining the median and the range of the overall precision values, because:
   - the error in the concentration measurement was too large (marked with brackets);
   - for the determination of the repeatability less than 5 laboratories where found for which in <u>both</u> duplicate leaching tests using the procedure 8.3 clearly a leaching mechanism could be determined (marked *). For the determination of the reproducibility always the results of at least 8 laboratories could be used.

The round-robin on the above materials and components combinations have the following values for standard deviations for repeatability (S_r) and reproducibility (S_R) in the diffusion test.

	Median	**Range**
S_r in the determination of ε_{64}	13%	8% to 18%
S_R in the determination of ε_{64}	16%	10% to 42%
S_r in the determination of pD_e (unit: -log[m^2/s])	0.11	0.07 to 0.17
S_R in the determination of pD_e (unit: -log[m^2/s])	0.19	0.12 to 0.40

In general no clear dependency of S_r and S_R on the material type was found.

NOTES:

1 No correction is made for the contribution of the analytical error, because ε_{64} and pD_e are calculated using a diffusion model through a fitting procedure. In general, the influence of the analytical error is of minor importance in the above values of the precision.

2 The precision values for the diffusion test are corrected for the error in the availability test result.

3 The values for Sr and S_R shown are only appropriate for material-component combinations for which:

- the contribution of the relative standard deviation in the concentration measurement is less than 5%.
- at least 5 data sets are available for which clearly a diffusion controlled leaching mechanism could be determined.

All material-component combinations in table A.1 that are not marked with brackets or *, satisfy these two requirements.

The mentioned median values and ranges for S_r and S_R are indicative values of the attainable precision, if the diffusion test is performed according to this standard and also the requirements mentioned in note 3 above are met. In particular, a higher degree of uncertainty may apply to materials which are very heterogeneous and/or to components for which the concentration measurements in the eluate causes problems (due to e.g. low levels).

Annex B (Informative)

Differences between NEN 7375 and NEN 7345

The repeatability and reproducibility of the diffusion test according to NEN 7345, established in the round-robin validation test (see Annex A of this standard), proved less good than desired. For this reason, under the auspices of the Action Programme Normalisation and Validation of Environmental Measurement Methods a project *Improvement of the quality of three normalised leaching tests in the NEN-7340 series* (ANVM-216,) was undertaken. In that project, consideration was also given to the developments on European harmonisation under the auspices of the CEN committee TC 292. Most of the changes proposed in ANVM-216 for undertaken diffusion tests have been adopted by the standards committee 390 011 and recommended for adoption in the standard. The existing standard NEN 7345 will not be revised because at this time CEN/TC 292 diffusion tests for earthy and stony waste materials are being developed, so there is a “stand still” on the development of national standards on the same subject. At the same time, it is expected that NEN 7345 will be replaced by one or more of the CEN/TC 292 developed standards for diffusion tests. Because in the meantime there is still a need for a generally applicable diffusion test, in which the recommendations from project ANVM-216 are adopted, a new standard (NEN 7375) has been brought out with a wider applicability than CEN is considering, namely all earthy and stony materials.

The most important changes from NEN 7345 that have been brought forward in NEN 7375 are as follows:

1. The applicability is generalised to earthy and stony materials (as opposed to just earthy and stony building materials and wastes).
2. The diffusion test must in future be conducted with pH neutral instead of acidified water. The most important reason for this is that this will be incorporated in the standards being developed in CEN/TC 292.

   An additional advantage of this is that the use of pH neutral water is that, in the case of materials with a low buffering capacity, large differences in the initial leaching by leaching fluid with an imposed pH=4 is overcome. This effect is much less with the use of pH neutral water. A separate literature and model study has considered the consequences of using neutral instead of acidified water. This has found that the difference in leaching results are possibly only observed in materials with a very low buffering capacity. Examples of this are vitrified slag, some industrial slags and sintered products, such as artificial gravel and brick. The differences in leaching for these types of material also appear to be very small (and only observed for metals); under normal laboratory conditions these are barely discernable.
3. The “paper method” has been introduced for the determination of the geometric surface area of highly irregular test pieces.
4. The determination of the leaching mechanism during the diffusion test is more systematically described and elaborated
5. The leaching volume is smaller, thus the required determination limit in testing to (regulatory) standards is easier to achieve analytically.
6. The “diffusion controls the leaching from the matrix” as criterion for applicability of the standard is replaced with the criterion “no dissolution of the matrix”.
7. For the calculation of the cumulative leaching per unit surface area, it is no longer necessary to undertake the availability test according to EA NEN 7371, since the value of the diffusion coefficient derived from that test has been eliminated from formulas (7) and (9) for the arithmetic leaching of a component over a given interval ($\varepsilon_{x,y}$) and over a period of 64 days (ε_{64}), respectively.

8. For the determination of the average negative logarithm of the effective diffusion coefficient per component, it is still necessary to undertaken the availability test according to EA NEN 7371. This determination is set out in an informative annex (Annex D.1).
9. For the determination of the leaching per component, for which according the procedure in 8.3.4 no diffusion controlled leaching can be established, whilst according to 8.3.3 it is established that the matrix does not dissolve, a calculation method is given to establish the upper limit of leaching.

Annex C

Commentary on the Prescribed Test Pieces and Determination of the Geometric Area

C.1 It is recommended that at least three test pieces are available, two of which meet the dimensional requirements, as supplementary tests may be found necessary. The third test piece may be necessary for performance of an availability test according and is finely ground for this.

C.2 In general, diffusion is determined on the basis of leaching from the entire test piece. This may be a sample of an original building element (e.g. a brick) or a test piece moulded in a special mould from the material to be tested (e.g. a Marshall slab of asphalt concrete).

C.3 To prevent practical problems in the performance of the test, it is recommended that an upper limit of 300 mm be set for the largest dimension of the test piece.

C.4 To prevent the leaching diminishing during the diffusion test due to depletion of a component, the smallest dimension of the test piece must be larger than 40 mm. For components with great mobility, during the test some depletion can occur if the smallest dimension lies in the area of the lower limit of 40 mm. Depletion of mobile components can then be prevented by using a slightly larger test piece.

C.5 Certain building materials are produced as standard with a thickness of less than 40 mm such as slate roof covering, ceramic roof tiles, thin tiles, hollow bricks or garden tiles. Usually the required strength of these products implicitly leads to materials with such a high pD_e value that no depletion phenomena occur during the diffusion test. For an optimum result in the diffusion test, such thin test pieces must be covered on one side.

C.6 For partial covering of a test piece with an impervious layer, material must be used that has no disruptive influence on the diffusion process by the release, absorption or (delayed) transmission of components to be studied. It has appeared that acrylic resin is a suitable impervious material for leaching tests on inorganic components with the diffusion test. The usability of other impervious materials is still being studied.

C.7 The test piece can be prepared in the laboratory under conditions that correspond to those found in practice. Preference is however given to the product as used in practice. The test piece can also be part of the manufactured product unless surface treatment causes significant differences in the surface structure or the ground surface. The latter can be compensated by covering the surface concerned such that no rinsing or diffusion from the surface occurs during the test.

C.8 If, after production, the product must harden for a specific period before reaching the strength required in practice, it is important for the interpretation of the results of the diffusion test to bear in mind that also the leaching behaviour can change during the period that hardening takes place.

C.9 Some test pieces are sawn or drilled out of a larger whole, for example a drilling core from a road surface. The sides formed by the sawing or drilling may have leaching extent not shown by the unworked surfaces. The worked surfaces must be covered in accordance with the procedure in Section 7.2.2. For a number of materials, it has been found that the diffusion differs little or not at all from the diffusion from the unworked part. In these cases, the sawn or drilled surfaces can also be included in determining the diffusion.

C.10 If the geometric area cannot be clearly and easily established for the entire surface, the test can often be carried out on part of the outer surface. Examples of materials where part of the surface must be covered are coarse slag and cobbles. Often one or more test pieces are selected from a representatively assembled sample of such slag or cobbles, for which large parts have an area that can be easily determined geometrically.

Partial covering may also be necessary for certain products with a regular and easily definable geometric area, for example roof tiles (with edges and rounded corners) or grass tiles (with gaps). Hollow building materials must have the holes filled with an impervious material.

Some building materials have different properties on different sides, e.g. if glazed layers or paint are applied. In these cases, the type of material surface to be studied is isolated by covering the other surfaces.

Annex D

Assessment of a Diffusion Coefficient and Calculation of Derived Values

D.1 Assessment of the effective diffusion coefficient of a component

The effective diffusion coefficient of a component can only be calculated when, through the procedure given in 8.3.3 and also the increment analysis in 8.3.2, it can be shown the leaching is diffusion controlled, and when for this material the available leaching quantity is known. For this the following procedure must be followed:

Calculate the average effective diffusion coefficient D_e of a component with the formula:

$$D_e = \left(\frac{\varepsilon_{64}}{2653 \times \rho \times U_{avail}} \right)^2 \times f \qquad \text{(D.1)}$$

where:

D_e is the average, effective diffusion coefficient for a given component, in m^2/s;
ε_{64} is the derived cumulative leaching of the component over 64 days determined with formula (9), in mg/m^2;
ρ is the density of the test piece, in kg dry matter per m^3;
U_{avail} is the leachable available quantity derived according to EA NEN 7371, in mg per kg dry matter
f is a factor equal to 1 s^{-1}.

Also express the average value of the effective diffusion coefficient in the form of a negative logarithm:

$$pD_e = -\log D_e \qquad \text{(D.2)}$$

D.2 Assessment of a diffusion coefficient

The value of pD_e indicates the rate of leaching. The minimum value of pD_e (maximum rate of leaching) for a component such as sodium is equal to 8.88 (free mobility of sodium in water).

The higher the pD_e value, the lower the speed of leaching of the component concerned with constant availability U_{avail} (this determines the concentration gradient which is the driving force for diffusion):

$pD_e > 12.5$:component with low mobility;
$11.0 < pD_e < 12.5$:component with average mobility;
$pD_e < 11.0$:component with high mobility.

A pD_e value of less than 9.5 has no physical significance as the material to be studied has no further internal porosity (tortuosity). If such a low value is found in the calculation, it is advisable to check the availability measured.

D.3 Comparison of the mobility of a component in a moulded or monolithic material with the free mobility of sodium in water

Tortuosity is a measurement of physical retardation and gives an indication of the path length that a diffusing ion must cover in a porous matrix. It is a material property and therefore not ion-dependent. For calculation of the tortuosity, a component must be selected that has no chemical interaction with the matrix. This component will show the lowest pD_e value in the matrix concerned. In most cases, sodium is the best choice.

The tortuosity of a moulded or monolithic material can be calculated using the formula:

$$T = \frac{D_{Na}}{D_{e,Na}} \qquad \text{(D.3)}$$

where:

T	is the tortuosity of the material;
D_{Na}	is the diffusion coefficient of sodium in water ($10^{-8.88}$) in m^2/s;
$D_{e,Na}$	is the effective diffusion coefficient of sodium in the material in m^2/s.

The retention factor is an indicator of the chemical retention of a component in a moulded or monolithic material. For a component that shows no interaction with the material matrix, this is equal to 1.

The retention factor (R) for the component concerned can be calculated using the formula:

$$R = \frac{D}{D_e \times T} \qquad \text{(D.4)}$$

where:

R	is the retention factor;
D	is the diffusion coefficient for the component in water in m^2/s;
D_e	is the effective diffusion coefficient for the component in the material in m^2/s;
T	is the tortuosity of the material.

D.4 Determination of the leached quantity per unit mass in the diffusion test

The quantity of a component leached out per mass unit up to a time t can be calculated using the formula:

$$U_{dif,t} = \frac{2 \times A \times \rho \times U_{avail} \times \sqrt{\frac{D_e \times t}{\pi}}}{m} \qquad \text{(D.5)}$$

where:

$U_{dif,t}$	is the quantity of a component leached out in the diffusion test to time t in mg per kg dry matter;
U_{avail}	is the quantity of component available for leaching in mg per kg dry matter;
D_e	is the effective diffusion coefficient of the component in m^2/s;
t	is the time duration of the leaching in s;
A	is the area of the test piece in m^2;
ρ	is the density of the test piece in kg dry matter per m^3;
m	is the mass of the test piece in kg dry matter.

From the leached quantities of a specific component as calculated in formula (17), and the content of the component available in the test piece, the extent of depletion can be approximated. For this, the relative leaching in the diffusion test must be calculated using the formula:

$$UP_{dif,t} = \frac{U_{dif,t}}{U_{avail}} \times 100\% \qquad \text{(D.6)}$$

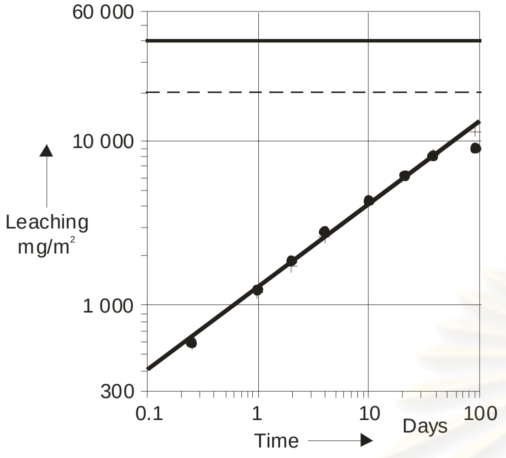
where:

$UP_{dif,t}$	is the percentage of leached component in time t of the diffusion test in relation to the available content in the test piece
$U_{dif,t}$	is the leached quantity of the component in time t of the diffusion test in mg per kg dry matter;
U_{avail}	is the quantity of the component available for leaching in mg per kg dry matter.

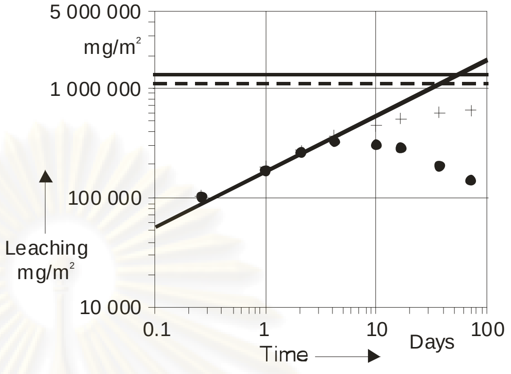
Annex E (informative)

Graphical representation of diffusion controlled leaching in special cases.

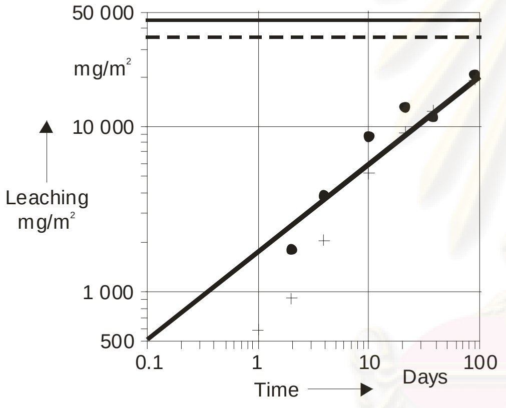
E.1 Diffusion Controlled Leaching



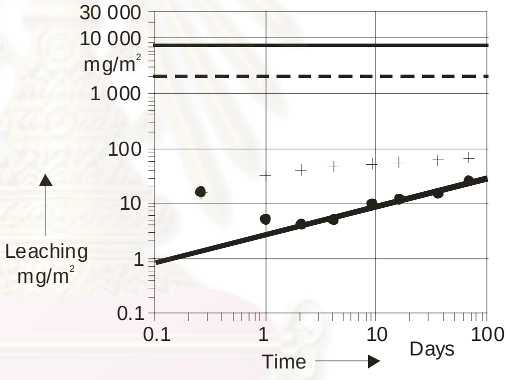
E.2 Depletion of Mobile Component



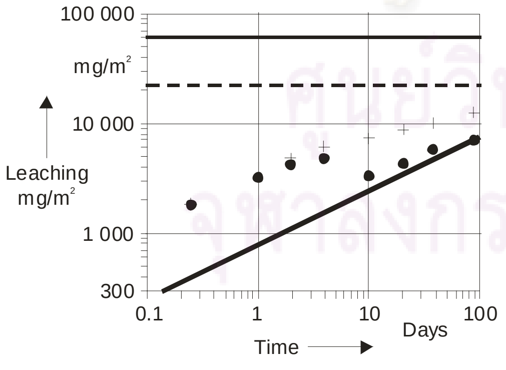
E.3 Delayed Leaching



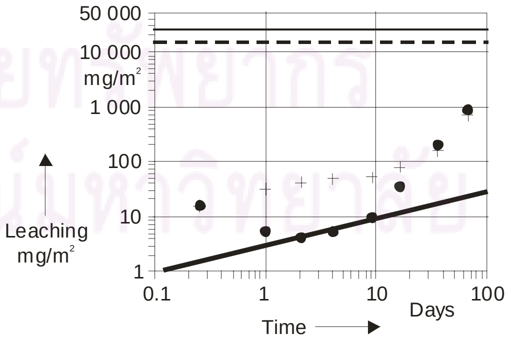
E.4 Surface Wash-off



E.5 Changing Release Mechanisms



E.6 Changes in Redox Conditions



KEY

\+ Cumulative measured leaching, from 8.2.1 equation (4)

● Cumulative measured leaching, from 8.2.2 equation (5)

━━ Slope defined by rc=0.5

—— Upper limit defined by total content of component

\- - - - Upper limit based on availability in accordance with NEN 7371

Annex F

Explanation of the calculation of the upper limit for leaching in special cases

If a material behaves as a porous matrix, it may be assumed that all components evenly distributed in the matrix basically leach diffusion controlled. Even for this type of material it is not always possible to demonstrate for each component a diffusion controlled release using procedure 8.3.4. This occurs mainly in components that only have a low availability and/or a high pD_e value. Also other factors like wash-off, dissolution of only the outer layer of the moulded or monolithic material, chemical specification, complex eluate compositions etc. can lead to no diffusion coefficient being determined for specific components.

In some cases also for components for which no diffusion coefficient could be determined according to 8.3.4, it is possible to give an indication of the cumulative release to be expected based on the results of the diffusion test. For 5 special cases formulas are given in 8.6 of this standard to estimate the upper limit of leaching after a time period of 64 days and for any given time period T (>64 days), respectively. The leaching ε_T after T days will always be calculated from the ε_{64} value using a factor $\sqrt{(T/64)}$. Partly caused by the restrictions of the one-dimensional diffusion model it can occur that the calculated upper limit in this way is substantially larger than the available amount for the object under investigation given by the formula:

$$\varepsilon_b = U_{avail} \text{ x } \rho \text{ x } d \qquad \text{(F.1)}$$

where:

ε_b is the calculated cumulative release of a component in the object under investigation, in mg dry matter per m^2;

U_{avail} is the available amount for leaching in mg/kg dry matter;

ρ is the density of the test piece in kg dry matter per m^3;

d is the thickness of material under investigation in m.

If it is found that ε_b is smaller than ε_T then the value of ε_b should be taken as the best estimate of the upper limit.

If a more precise insight into the level of leaching is required than an indicative upper limit, the diffusion test must be carried out with more accurate analysis instruments, a longer test duration, longer periods between replacement or a lower fluid-volume ratio. This standard does not give instructions for this as the approach is not normally considered necessary.

APPENDIX H

Heavy metals analysis

Table H-1 Heavy metal content in clinker 1

Time	Clinker condition	% Sludge	Mg	Mn	Na	Ni	Pb	Sr	Tl	V	Zn
60	1100	0	123.58	108.42	76.05	64.40	234.14	174.94	95.16	128.41	345.90
60	1100	0.5	124.74	117.03	82.21	100.44	242.16	134.77	120.01	107.25	279.04
60	1100	1	541.56	183.51	41.77	110.43	42.43	610.74	168.45	164.62	159.73
60	1100	1.5	169.59	151.95	63.35	77.49	171.58	229.14	29.81	160.94	309.56
60	1100	2	180.55	122.37	86.07	51.21	224.55	229.00	133.16	157.80	331.27
60	1200	0	232.90	74.40	23.97	40.96	23.23	244.42	187.79	70.25	87.03
60	1200	0.5	2.11	2.12	1.32	8.94	29.91	0.38	88.88	2.88	30.62
60	1200	1	2.00	2.79	2.56	17.01	62.83	0.40	90.46	3.22	32.04
60	1200	1.5	86.14	64.54	42.04	42.53	90.07	92.75	62.76	70.14	197.46
60	1200	2	44.39	52.46	91.48	43.60	193.18	27.39	78.44	65.39	207.54
60	1300	0.5	250.46	64.07	39.43	24.48	24.54	214.97	201.86	74.84	100.57
60	1300	1	104.81	84.91	72.74	88.34	71.54	107.19	154.37	92.80	205.15
60	1300	1.5	89.33	67.05	48.14	37.03	40.09	119.93	45.07	80.22	215.40
60	1300	2	89.75	112.93	54.99	141.73	63.59	65.34	142.63	76.60	222.12
60	1300	2.5	124.21	72.29	50.83	55.78	43.98	128.22	103.41	92.39	123.64
60	1300	3	98.82	133.09	38.12	176.99	38.27	104.93	63.43	67.89	188.31
60	1350	0	325.97	144.53	46.93	108.25	17.32	296.01	133.40	101.03	120.16
60	1350	0.5	76.71	120.62	63.22	148.71	68.39	84.28	86.38	91.67	260.77
60	1350	1	88.60	76.52	74.10	82.03	83.79	83.44	112.56	83.89	242.52
60	1350	1.5	104.38	115.21	68.13	106.58	69.00	112.51	106.29	108.66	258.37
60	1350	2	96.29	219.87	72.69	472.54	88.24	81.69	72.33	94.24	275.44
60	1350	2.5	118.11	136.45	81.10	163.05	63.97	131.84	126.15	132.80	116.19
60	1350	3	141.01	132.07	76.01	135.24	37.11	148.72	142.40	132.41	113.11
60	1400	0	336.61	169.99	36.72	130.80	15.53	338.70	199.36	136.65	107.69
60	1400	0.5	128.02	144.59	48.04	123.88	64.93	125.53	111.14	112.31	257.37
60	1400	1	101.63	129.87	58.25	144.53	34.53	121.26	49.81	103.89	143.85
60	1400	1.5	103.02	107.38	62.39	86.68	55.91	90.77	119.27	101.36	171.29
60	1400	2	104.20	117.01	38.44	119.10	83.85	97.51	138.49	108.71	292.99
60	1400	2.5	111.10	61.21	53.16	24.83	139.82	120.12	46.48	118.43	300.39
60	1400	3	135.26	154.33	36.58	140.07	25.84	143.76	66.45	142.69	112.66

Table H-2 Heavy metal content in clinker 2

Time	Clinker condition	% Sludge	Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Li
60	1100	0	74.88	159.40	74.49	63.86	29.09	482.70	112.26	102.65	119.61
60	1100	0.5	112.45	105.66	72.22	31.25	119.58	478.80	139.30	61.48	106.46
60	1100	1	128.57	80.43	300.43	111.09	198.07	168.89	209.47	82.20	98.01
60	1100	1.5	144.69	123.82	100.64	99.61	57.34	513.67	152.65	108.18	113.07
60	1100	2	184.40	112.17	233.57	111.31	55.55	388.28	121.39	80.18	216.00
60	1200	0	58.04	30.87	363.28	30.33	57.22	94.34	79.74	69.75	66.13
60	1200	0.5	63.96	0.12	4.61	15.49	2.51	40.21	3.96	0.87	2.21
60	1200	1	65.11	0.11	4.27	24.63	8.34	53.87	4.98	0.48	4.10
60	1200	1.5	77.78	48.61	81.63	63.16	26.37	311.98	62.16	85.77	64.89
60	1200	2	83.62	8.81	159.51	120.69	31.97	244.03	48.01	78.18	175.13
60	1300	0.5	40.51	53.44	127.72	32.99	23.46	93.55	54.77	61.49	57.15
60	1300	1	51.95	80.68	134.64	48.76	67.27	245.99	69.26	78.89	114.48
60	1300	1.5	63.01	59.57	269.95	49.83	33.29	279.26	75.78	65.09	104.59
60	1300	2	66.89	51.21	87.43	48.99	143.79	379.42	110.02	77.89	78.80
60	1300	2.5	78.03	71.42	144.81	45.80	57.06	154.59	79.19	42.04	119.29
60	1300	3	78.48	49.22	76.78	48.48	191.77	392.85	145.78	84.56	71.53
60	1350	0	38.55	29.28	351.40	27.91	177.46	133.75	136.17	105.59	81.02
60	1350	0.5	42.78	65.25	91.26	54.53	122.48	440.09	72.18	63.16	106.30
60	1350	1	51.88	60.65	0.06	63.99	62.77	356.73	87.41	71.13	93.72
60	1350	1.5	57.46	59.47	310.58	75.49	105.73	396.70	115.43	65.13	175.84
60	1350	2	70.16	54.99	92.42	57.44	728.25	646.78	204.42	53.84	151.90
60	1350	2.5	73.08	96.60	120.88	66.42	136.59	147.52	110.66	95.35	144.93
60	1350	3	79.55	86.62	139.97	52.99	133.83	159.95	128.98	77.11	165.04
60	1400	0	35.36	56.46	400.45	27.99	200.47	112.49	141.15	92.25	103.44
60	1400	0.5	52.23	59.55	307.07	54.77	145.88	407.87	152.90	63.98	203.67
60	1400	1	56.84	57.48	131.29	37.40	146.59	267.61	111.00	73.60	129.02
60	1400	1.5	58.27	74.48	101.69	35.31	74.84	274.36	91.49	75.52	122.24
60	1400	2	67.25	46.90	100.81	28.57	121.77	567.38	111.83	49.10	167.49
60	1400	2.5	71.07	71.60	134.61	94.70	11.78	186.65	43.17	83.09	95.74
60	1400	3	77.48	47.39	140.48	44.55	147.55	166.46	115.58	64.03	196.37

Table H-3 Sequential extraction test in clinker

Al	M0	M1	M2	Ca	M0	M1	M2	Cd	M0	M1	M2	Cr	M0	M1	M2	Cu	M0	M1	M2
F1	0.552	0.6477	7.1778	F1	0.5016	0.2433	1.9982	F1	0.014	0.034	1.090	F1	0.446	1.133	3.108	F1	0.013	0.006	0.044
F2	0.433	0.4562	1.8075	F2	1.893	0.2276	1.9838	F2	0.011	0.026	1.585	F2	0.003	1.460	2.550	F2	0.005	0.003	0.100
F3	0.245	0.0464	1.6295	F3	1.9626	0.8904	7.5222	F3	0.104	0.201	1.525	F3	0.024	1.275	2.037	F3	1.107	0.220	1.620
F4	3.188	23.733	25.932	F4	2.0844	0.9758	8.1215	F4	0.879	2.069	6.354	F4	0.206	4.868	5.034	F4	0.355	0.532	2.253
F5	95.582	75.117	63.453	F5	93.558	97.663	80.374	F5	98.991	97.671	89.446	F5	99.320	91.264	87.271	F5	98.519	99.238	95.984
Fe	M0	M1	M2	K	M0	M1	M2	Li	M0	M1	M2	Mg	M0	M1	M2	Mn	M0	M1	M2
F1	0.266	0.12	0.010	F1	13.264	14.928	15.126	F1	0.291	0.481	0.948	F1	8.384	8.299	8.290	F1	0.013	0.003	0.076
F2	0.049	0.05	0.037	F2	5.572	6.049	8.435	F2	0.124	0.196	0.755	F2	3.560	5.796	6.666	F2	0.078	0.001	0.007
F3	20.158	22.42	25.043	F3	45.415	48.913	45.748	F3	3.331	4.059	4.514	F3	8.182	8.417	10.251	F3	10.404	15.813	14.498
F4	4.326	6.29	8.538	F4	21.370	22.049	25.827	F4	1.579	2.704	2.820	F4	40.557	40.591	46.363	F4	2.097	5.061	7.526
F5	75.202	71.124	66.372	F5	14.380	8.060	4.863	F5	94.674	92.560	90.964	F5	39.317	36.897	28.429	F5	87.406	79.123	77.893
Na	M0	M1	M2	Ni	M0	M1	M2	Pb	M0	M1	M2	V	M0	M1	M2	Zn	M0	M1	M2
F1	1.048	1.969	2.126	F1	0.353	0.061	0.069	F1	0.101	0.128	0.212	F1	0.028	0.004	0.048	F1	0.014	0.015	0.109
F2	21.347	23.555	24.464	F2	0.073	0.012	1.087	F2	0.074	0.210	0.741	F2	0.011	0.003	0.218	F2	0.006	0.004	0.247
F3	40.270	43.272	45.310	F3	0.958	0.485	1.177	F3	0.559	0.935	1.068	F3	0.081	0.692	0.753	F3	0.138	0.070	1.576
F4	15.300	19.481	20.376	F4	3.074	4.141	5.345	F4	0.506	0.243	1.335	F4	1.165	1.234	8.001	F4	4.222	8.484	11.528
F5	22.035	11.724	7.724	F5	95.542	95.301	92.323	F5	98.760	98.484	96.645	F5	98.715	98.068	90.979	F5	95.621	91.428	86.540

Table H-4 Sequential extraction test in cement paste

Al	M0	M1	M2	Ca	M0	M1	M2	Cd	M0	M1	M2	Cr	M0	M1	M2	Cu	M0	M1	M2
F1	0.937	0.750	0.106	F1	0.62	1.16	1.70	F1	0.131	0.141	0.103	F1	0.018	1.511	0.115	F1	0.076	0.157	0.102
F2	0.226	1.976	0.255	F2	0.60	1.14	1.71	F2	0.132	0.057	0.096	F2	0.013	0.904	0.057	F2	0.058	0.094	0.051
F3	2.543	1.093	2.687	F3	0.66	1.32	1.89	F3	0.303	0.221	0.171	F3	0.764	3.229	2.309	F3	3.303	3.515	2.048
F4	1.357	0.116	0.712	F4	0.07	0.16	0.20	F4	0.154	0.557	0.506	F4	0.011	0.584	0.049	F4	0.046	0.061	0.043
F5	94.937	96.065	96.241	F5	98.049	96.226	94.492	F5	99.280	99.024	99.124	F5	99.195	93.772	97.469	F5	96.517	96.175	97.756
Fe	M0	M1	M2	K	M0	M1	M2	Li	M0	M1	M2	Mg	M0	M1	M2	Mn	M0	M1	M2
F1	0.011	0.01	0.007	F1	11.797	21.642	36.003	F1	3.621	4.122	7.427	F1	0.108	0.147	0.219	F1	0.007	0.036	0.023
F2	0.021	0.00	0.008	F2	4.193	7.810	12.927	F2	1.192	0.979	1.785	F2	0.092	0.123	0.183	F2	0.008	0.028	0.022
F3	10.183	9.05	7.877	F3	6.965	10.768	25.130	F3	6.279	5.223	13.631	F3	0.106	0.159	0.220	F3	14.955	19.619	31.595
F4	0.017	0.01	0.011	F4	0.136	0.249	0.466	F4	0.207	0.207	0.399	F4	0.004	0.008	0.013	F4	0.008	0.045	0.034
F5	89.768	90.933	92.097	F5	76.908	59.531	25.473	F5	88.701	89.469	76.758	F5	99.689	99.563	99.365	F5	85.022	80.272	68.326
Na	M0	M1	M2	Ni	M0	M1	M2	Pb	M0	M1	M2	V	M0	M1	M2	Zn	M0	M1	M2
F1	0.371	0.414	0.583	F1	0.995	0.823	0.937	F1	0.696	1.151	1.311	F1	0.047	0.068	0.114	F1	0.001	0.050	0.006
F2	7.760	8.738	10.808	F2	0.341	0.227	0.265	F2	0.401	0.607	0.674	F2	0.028	0.040	0.086	F2	0.001	0.047	0.005
F3	3.440	3.732	5.222	F3	0.318	0.659	0.528	F3	0.864	0.973	1.251	F3	1.951	3.175	6.759	F3	0.007	0.585	0.045
F4	0.105	0.115	0.192	F4	1.821	3.590	5.127	F4	1.095	1.474	1.685	F4	0.012	0.024	0.038	F4	0.000	0.030	0.005
F5	88.323	87.001	83.196	F5	96.525	94.701	93.143	F5	96.944	95.795	95.079	F5	97.962	96.694	93.002	F5	99.991	99.288	99.938

Table H-5 Sequential extraction test in cement mortar

Al	M0	M1	M2	Ca	M0	M1	M2	Cd	M0	M1	M2	Cr	M0	M1	M2	Cu	M0	M1	M2
F1	0.00	0.00	0.00	F1	0.21	0.03	0.02	F1	0.190	0.120	0.116	F1	0.801	0.796	0.681	F1	0.881	0.606	0.867
F2	0.00	0.00	0.00	F2	0.17	0.02	0.02	F2	0.093	0.182	0.066	F2	0.392	0.509	0.596	F2	0.431	0.387	0.760
F3	0.05	0.03	0.07	F3	0.16	0.02	0.02	F3	0.362	0.426	0.288	F3	1.940	0.734	1.120	F3	21.328	5.594	14.270
F4	0.00	0.00	0.01	F4	0.00	0.00	0.02	F4	0.128	0.379	0.351	F4	0.425	0.172	1.932	F4	0.467	0.131	2.462
F5	99.95	99.97	99.92	F5	99.452	99.930	99.923	F5	99.226	98.894	99.178	F5	96.443	97.789	95.671	F5	76.893	93.281	81.640
Fe	M0	M1	M2	K	M0	M1	M2	Li	M0	M1	M2	Mg	M0	M1	M2	Mn	M0	M1	M2
F1	0.006	0.01	0.012	F1	18.657	20.458	23.815	F1	0.141	0.391	0.300	F1	0.225	0.271	0.304	F1	0.029	0.068	0.069
F2	0.004	0.01	0.057	F2	5.992	7.734	8.466	F2	0.047	0.139	0.094	F2	0.188	0.241	0.265	F2	0.025	0.124	0.063
F3	8.530	3.83	9.481	F3	8.281	4.567	10.813	F3	0.256	0.503	0.651	F3	0.179	0.211	0.326	F3	9.549	7.670	15.307
F4	0.012	0.01	0.971	F4	0.067	0.044	2.323	F4	0.004	0.012	0.281	F4	0.004	0.022	0.324	F4	0.032	0.141	1.095
F5	91.449	96.149	89.480	F5	67.003	67.196	54.584	F5	99.552	98.955	98.674	F5	99.404	99.254	98.781	F5	90.365	91.997	83.465
Na	M0	M1	M2	Ni	M0	M1	M2	Pb	M0	M1	M2	V	M0	M1	M2	Zn	M0	M1	M2
F1	0.958	1.007	1.029	F1	0.257	0.319	0.278	F1	1.191	1.442	1.240	F1	0.116	0.142	0.147	F1	0.004	0.002	0.456
F2	25.360	24.949	26.500	F2	0.847	0.118	0.106	F2	0.503	0.741	0.713	F2	0.016	0.039	0.065	F2	0.002	0.001	0.198
F3	9.257	7.171	11.212	F3	0.340	0.201	0.263	F3	1.428	1.706	2.260	F3	8.307	7.649	13.587	F3	0.064	0.025	1.178
F4	0.136	0.065	2.866	F4	3.459	3.003	3.746	F4	1.435	0.977	0.739	F4	0.080	0.120	7.380	F4	0.002	0.001	2.409
F5	64.289	66.808	58.392	F5	95.097	96.359	95.606	F5	95.443	95.134	95.047	F5	91.481	92.050	78.821	F5	99.928	99.970	95.760

BIOGRAPHY

Miss Thantip Punmatharith was born on October 26, 1980 in Bangkok, Thailand. She graduated with a Bachelor of Science in Environmental Science from Silpakorn University in 2002. After that, she received her Master Degree in Environmental Management from Inter-Departmental Program in Environmental Management, Chulalongkorn University in 2005. She pursued her Degree of Doctor of Philosophy in Environmental Management in Inter-Departmental Program in Environmental Management, Chulalongkorn University in 2006. She finished her Doctoral Degree of Philosophy in Environmental Management in August 2009.