EFFECT OF Cr, Ni, Cu AND Zn IN CLINKER ON PHYSICAL PROPERTIES OF CEMENT VIA CO-PROCESSING IN A PILOT-SCALE ROTARY CEMENT KILN

Mr. Jenwit Krobthong

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2011

ผลของโครเมียม นิกเกิล ทองแดง และสังกะสี ในปูนเม็ดที่มีต่อสมบัติทางกายภาพของปูนซีเมนต์โดยกระบวนการเผาร่วมในเตาเผาปูนซีเมนต์จำลอง

นายเจนวิทย์ กรอบทอง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2554

Thesis Title	EFFECT OF Cr, Ni, Cu AND Zn IN CLINKER ON PHYSICAL PROPERTIES OF CEMENT VIA CO-PROCESSING IN A PILOT-SCALE ROTARY CEMENT KILN
By	Mr. Jenwit Krobthong
Field of Study	Environmental Management
Thesis Advisor	Assistant Professor Manaskorn Rachakornkij, Ph.D.
Thesis Co-advisor	Assistant Professor Viboon Sricharoenchaikul, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

……………………………………Dean of the Graduate School
(Associate Professor Amorn Petsom, Ph.D.)

THESIS COMMITTEE

……………………………………Chairman
(Assistant Professor Chantra Tongcumpou, Ph.D.)

……………………………………Thesis Advisor
(Assistant Professor Manaskorn Rachakornkij, Ph.D.)

……………………………………Thesis Co-advisor
(Assistant Professor Viboon Sricharoenchaikul, Ph.D.)

……………………………………Examiner
(Assistant Professor Chakkaphan Sutthirat, Ph.D.)

…………………………………… Examiner
(Assistant Professor Pisut Painmanakul, Ph.D.)

……………………………………External Examiner
(Assistant Professor Pusit Lertwattanaruk, Ph.D.)

……………………………………External Examiner
(Thirarath Wongamatasiri, Ph.D.)

เจนวิทย์ กรอบทอง : ผลของโครเมียม นิกเกิล ทองแดง และสังกะสี ในปูนเม็ดที่มีต่อสมบัติทางกายภาพของปูนซีเมนต์ โดยกระบวนการเผาร่วมในเตาเผาปูนซีเมนต์จำลอง (EFFECT OF Cr, Ni, Cu AND Zn IN CLINKER ON PHYSICAL PROPERTIES OF CEMENT VIA CO-PROCESSING IN A PILOT-SCALE ROTARY CEMENT KILN) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. มนัสกร ราชากรกิจ, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.วิบูลย์ ศรีเจริญชัยกุล, 193 หน้า.

เตาเผาปูนซีเมนต์สามารถใช้สำหรับการทำลายของเสียทั้งจากสารอินทรีย์ที่เป็นอันตรายและการรักษาเสถียรภาพของโลหะหนัก วิธีการนี้จะช่วยให้ของเสียสามารถเป็นวัสดุทางเลือกที่เป็นวัตถุดิบหรือเชื้อเพลิงในกระบวนการผลิตปูนซีเมนต์ อย่างไรก็ตามโลหะหนักในกากของเสียมีผลกระทบต่อคุณสมบัติของปูนซีเมนต์ การศึกษานี้เป็นการศึกษาลักษณะทางเคมีและทางกายภาพของส่วนผสมต่างๆของปูนเม็ด วัตถุดิบถูกผสมด้วยอัตราส่วนที่แตกต่างกันจากออกไซด์ของโลหะหนัก: คือโครเมียม (3) ออกไซด์ (Cr_2O_3), คอปเปอร์ (2) ออกไซด์ (CuO), นิกเกิล (2) ออกไซด์ (NiO_2), และซิงค์ออกไซด์ (ZnO) สำหรับการผสมกันของโลหะหนักทั้งสี่ชนิดมีค่าระหว่าง 0.05-2.0% โดยน้ำหนัก ของส่วนผสมปูนซีเมนต์ปอร์ตแลนด์ ประเภท 1 ที่ถูกเผาไหม้ในเตาเผาปูนซีเมนต์จำลอง ซึ่งใช้ก๊าซปิโตรเลียมเหลวเป็นเชื้อเพลิง ผลการศึกษาพบว่าค่าความเข้มข้นของโลหะหนักในปูนเม็ดสูงกว่าในส่วนผสมก่อนที่จะเผาไหม้ นอกจากนี้โลหะหนักไม่ได้ถูกทำลายไปในกระบวนการการเผาไหม้และผลึกของโลหะหนักปรากฏอยู่ในปูนเม็ดซึ่งถูกฝังอยู่ใน C_2S, C_3S, C_3A และ C_4AF ความเข้มข้นของโลหะหนักที่เพิ่มขึ้นทำให้ร้อยละของแคลเซียมออกไซด์อิสระเพิ่มขึ้น แต่ร้อยละของ C_3S ลดลง โดยเฉพาะอย่างยิ่ง Cr และ Cu ความเข้มข้นมากกว่า 1.0% โดยน้ำหนักมีผลทำให้ร้อยละของแคลเซียมออกไซด์อิสระเพิ่มขึ้นมากกว่า 1.5% และทำให้ค่ากำลังรับแรงอัดลดลงต่ำกว่าเกณฑ์มาตรฐาน แต่สำหรับค่าความเข้มข้น Ni และ Zn ที่เพิ่มขึ้นค่าร้อยละของแคลเซียมออกไซด์อิสระเพิ่มขึ้นเล็กน้อยแต่ยังต่ำกว่า 1.5% อีกทั้งทำให้ค่ากำลังรับแรงอัดดีขึ้นสูงกว่าเกณฑ์มาตรฐาน โดยที่การปรับปรุงค่ากำลังรับแรงอัดสูงสุดที่ 1 วัน ที่ 0.05 %, 0.1%, 0.1% และ 0.5% โดยน้ำหนัก ของส่วนผสมของโลหะหนัก, Cu, Zn และ Ni ตามลำดับได้มากกว่า 130 กก. ซม.$^{-2}$ ค่ากำลังรับแรงอัดที่ 28 วันจากปูนเม็ดที่มีอยู่ 0.05-0.3%, 0.1%, 0.5% และ 1.0% โดยน้ำหนัก ของส่วนผสมของโลหะหนัก, Cu, Ni และ Zn ตามลำดับไม่น้อยกว่า 400 กก. ซม.$^{-2}$ แต่ผลการทดสอบการชะละลายได้แสดงให้เห็นว่าทั้งหมดของอัตราส่วนที่แตกต่างกันของโลหะหนักในปูนเม็ดและปูนซีเมนต์ยังอยู่ในช่วงมาตรฐานเมื่อเทียบกับมาตรฐานของไทย (Cr, Cu, Ni และ Zn ไม่เกิน 5, 25, 20 และ 250 ส่วนในล้านส่วน ตามลำดับ)

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม

5287785020 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORD: PILOT-SCALE ROTARY CEMENT KILN, CO-PROCESSING, HAZARDOUS WASTE, Cr, Ni, Cu, Zn, MECHANISMS OF HEAVY METAL.

JENWIT KROBTHONG: EFFECT OF Cr, Ni, Cu AND Zn IN CLINKER ON PHYSICAL PROPERTIES OF CEMENT VIA CO-PROCESSING IN A PILOT-SCALE ROTARY CEMENT KILN. ADVISOR: ASST. PROF. MANASKORN RACHAKORNKIJ, Ph.D., CO-ADVISOR: ASST. PROF. VIBOON SRICHAROENCHAIKUL, Ph.D., 193 pp.

Co-processing of industrial wastes in cement kiln can be used for both destruction of hazardous organics and stabilization of heavy metals. This method provides a management option to use the wastes as raw materials or fuel in cement production. However, heavy metals in the wastes may adversely affect cement properties. This study investigated chemical and physical characteristics of various mixtures of heavy metals in synthetic raw materials to produce cement clinkers. Raw materials were mixed with different ratios of single oxide of heavy metals: namely, chromium oxides (Cr_2O_3), copper oxides (CuO), nickel oxides (NiO_2), zinc oxide (ZnO), and the two combinations of four kinds of heavy metals, i.e. 0.05%, 0.3%, 0.5%, 1.0% and 2.0%. The mixtures of Ordinary Portland Cement Type I were burned in a pilot-scale rotary cement kiln which the liquefied petroleum gas was used as fuel. Results showed that concentrations of heavy metals in the clinkers were higher than those in the mixtures before combustion. Moreover, the heavy metals were not destroyed in the burning process and they were found in the clinker associated with main phases of clinker, C_2S, C_3S, C_3A and C_4AF. High concentrations of heavy metals caused increase in free lime content, but decrease in C_3S. In particular, Cr and Cu concentrations greater than 1.0% by weight were produced more than 1.5% of free lime and caused unacceptable compressive strengths. Increase in Ni and Zn concentrations caused free lime contents to increase slightly although they were still within the SCCC's quality standard of 1.5%. However, the mortars with higher Ni and Zn contents produced better compressive strength values than the standard values. Improvement of early strength at 1 day for 0.05%, 0.1%, 0.1% and 0.5% by weight of combination of heavy metals, Cu, Zn and Ni, respectively, were more than 130 kg cm^{-2}. The 28-day compressive strength values of clinkers containing 0.05-0.3%, 0.1%, 0.5% and 1.0% by weight of combination of heavy metals, Cu, Ni and Zn respectively, were more than 400 kg cm^{-2}. As for environmental impact evaluations, Waste Extraction Tests showed that heavy metal concentrations in leachates of all of the different ratios of heavy metals in clinker and cement mortar did not exceed the Thai regulatory standards (Cr, Cu, Ni and Zn less than 5, 25, 20 and 250 ppm respectively).

Field of Study Environmental Management Student's Signature

Academic Year 2011 Advisor's Signature

Co-advisor's Signature

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my thesis advisor, Assistant Professor Dr. Manaskorn Rachakornkij and my thesis co-advisor, Assistant Professor Dr. Viboon Sricharoenchaikul for their advice, guidance, kind support, and encouragement throughout this research.

I also would like to thanks Asst. Prof. Chantra Tongcumpou, Ph.D., Chairman of the committee, Asst. Prof. Chakkaphan Sutthirat, Ph.D. and Asst. Prof. Pisut Painmanakul, Ph.D., member, Asst. Prof. Pusit Lertwattanaruk, Ph.D. and Thirarath Wongamatasiri, Ph.D., external members of thesis committee for their invaluable suggestions and comments during this study.

I would like to thanks Mr. Thanit Pulivekin, Vice President of Technical & Engineering, Mr.Choompon Lertchuwongsa, Mr.Nattavude Kongmuang, Mr.Sampan, Mr.Wiwat and all concerns from the Siam City Cement Public Company Limited (SCCC) and 90th years anniversary Chulalongkorn University Ratchadaphisek Class 6 (2/2551) Research Fund for the grant, equipment, materials, and all involved information in this research. Support for this work was also provided by a grant from Center of Excellence for Environmental and Hazardous Waste Management. Without this scholarship, this research will not be achieved. Special thank to Hazardous Waste Laboratory, Department of Environmental Engineering, Chulalongkorn University for their instrumental supporting lab.

Next, I would like to thanks Dr. Thanthip for kindly supporting, especially Mr.Natt Dumkum and Mr. Nattara Tungkittithara, master degree students of Chulalongkorn University for helping on my research.

Finally, I feel proud to dedicate this thesis with due respect to my family and my friends for their supports and encouragement throughout my study.

CONTENTS

page

page

LIST OF TABLES

Table page

Table page

Table page

LIST OF FIGURES

Figure page

Figure page

CHAPTER I

INTRODUCTION

1.1 Research Motivation

The manufacturing industry generates both hazardous and non-hazardous wastes. Therefore, the proper treatment of waste is essential, particularly of hazardous wastes, which require complete and careful extermination. For example, some hazardous wastes need to undergo a destabilization process first, before being buried at a specific licensed, or secure, landfill. Some hazardous wastes, such as used oil, solvents, isopropyl alcohol, thinner, and acetone, need to be incinerated at high temperatures. The treatment and disposal of hazardous waste and non-hazardous waste can be carried out by means of incineration employing cement kiln technology (Punmatharith et al., 2010; Anonymous, 2006; Ract et al., 2003; Dalton et al., 2004). Cement kilns, which are operated at a high temperature of about 1450°C, are one of the well known methods for destruction of hazardous wastes and non-hazardous wastes and have been approved by the United States Environmental Protection Agency (U.S. EPA) and the Department of Industrial Works (DIW) of the Ministry of Industry, Thailand (Anonymous, 2006).

The use of hazardous waste incinerators and cement kilns are increasingly popular because they provide temperatures as high as 1450°, the heat level adequate for detoxifying any hazardous wastes. Cement kilns provide a new stability of cement products that leave no ash after incineration; the ash from the combustion of fuels or raw materials is incorporated into clinker or cement kiln dust (CKD). Most cement kiln operators normally return the majority of the CKD to the kiln to complete the calcination and burning processes. CKD also yields another benefit: it can serve as a waste recycling device by using residual engine oil as its fuel in place of coal. Additionally, some wastes, such as wastewater sludge, chemical-contaminated soil, and ash from the power plant, may be used as substitutes for raw materials and incinerated together with shale and limestone with high efficiency (Andrade et al., 2003; Ract et al., 2003; Punmatharith et al., 2010). Waste incineration in cement kilns is an exemplar model of environmental conservation, and the added advantage of it being a low-cost incineration option has made it a popular waste treatment method worldwide (Punmatharith et al., 2010; Holcim and GTZ, 2006; Ract et al., 2003; Sinyoung et al., 2011).

1.2 Research Objectives

The major objectives of this study are to investigate the effect of each heavy metal in clinker (OPC Type I). The following heavy metals will be analyzed in this study: Cr (Cr_2O_3), Cu (CuO), Ni (NiO_2) and Zn (ZnO). The four specific objectives of this research are as follows:

1) To analyze the components of heavy metals in raw materials (raw meal) before burning, in the clinker after burning them in a pilot-scale rotary cement kiln and in cement mortar with the following methods of testing: total on waste by the inductively couples plasma spectrometry (ICP) and Thai Regulatory Leaching Procedure as described in the Notification of Ministry of Industry B.E. 2548 on Management of Wastes at different concentrations of heavy metals in the mixture and the clinker.

2) To find the application concentration values of heavy metals in raw meal that can be burned by a pilot-scale rotary cement kiln which do not affect the quality of the clinker with the following methods of testing: ASTM C109/C109M-05.

3) To analyze the compounds and mechanism of heavy metals in the clinker at the maximum concentration values of heavy metals in the mixture with the following methods of testing: XRF, XRD and SEM.

4) To prepare equations in terms of the concentration of heavy metals in raw meal before burning and in the clinker after burning the mixture in a rotary cement kiln.

5) To focus in phase of clinker such as C_3S, C_2S, C_3A or C_4AF which contains heavy metals by SEM.

1.3 Hypothesis

After burning process, each heavy metal will be presented in clinker composition such as C_3S, C_2S, C_3A or C_4AF, which have impact on cement properties.

1.4 Scope of study

Various concentrations 0.05%-2.00% (% by weight) of each heavy metal and combination of heavy metals (metal oxide), Cr (Cr_2O_3), Cu (CuO), Ni (NiO_2) and Zn (ZnO) were mixed with a raw meal before burning. The component of heavy metals in the solid waste or mixture was analyzed with the ICP (total on waste) and the leaching procedure. After using a pilot-scale rotary cement kiln to burn the mixtures and turn them into clinker, the component of heavy metals in the clinker would also be analyzed with the ICP (total on waste) and Thai regulatory leaching procedure as described in the Notification of Ministry of Industry B.E. 2548 on Management of Wastes. The application concentration of each heavy metal in the mixture that they can be disposed of by cement kiln without affecting the quality of the clinker was considered with ASTM tests for strength as the following methods of testing: ASTM C109/C109M-05. The components and mechanisms of each heavy metal in the clinker at the maximum value of concentration were analyzed with the following methods of testing: XRF, XRD and SEM. After that, equations in terms of concentration of each heavy metal in the mixture before burning and in the clinker after burning were created to predict the concentration of heavy metals in the clinker in full scale rotary cement kiln.

1.5 Advantages of this work

1.5.1 A pilot-scale rotary cement kiln was constructed. Burning conditions set by the kiln resembled those of an actual kiln and produced cement of the same quality. This prototype was used to research the co-processing of wastes in the cement kiln.

1.5.2 Findings of this research were used to set up the standards for the maximum concentrations of heavy metals in raw meal for the purpose of hazardous waste disposal using cement kiln technology.

1.5.3 Findings of this research was used to create an equation that predicts the concentration of each heavy metal in a mixture before it is burned and in the clinker after it is burned in a full-scale rotary cement kiln.

1.5.4 Phase of clinker which contains heavy metals will be focused and discussed.

CHAPTER II

BACKGROUND

2.1 Introduction

The production of cement involves heating raw materials, typically limestone and clay (or shale), to approximately 1450°C to form clinker, which is cooled and then ground with a small amount of gypsum to produce cement. Limestone typically provides the calcium carbonate ($CaCO_3$), clay or shale provides the remaining components. If necessary, the silica (SiO_2), alumina (Al_2O_3), or iron oxide (Fe_2O_3) content of the raw materials can be supplemented by sand, bauxite, or an iron ore respectively. The proportions of the raw materials used depend on the type of cement that is being produced. Portland cement requires a limestone to clay ratio of about 3 to 1 (Environmental Toxicology International Inc., 1992).

The raw materials used in the cement production process naturally contain metals and halogens such as antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), vanadium (V), Zinc (Zn), bromine (Br), chlorine (Cl), fluorine (F), and iodine (I). The amounts of these components depend on the geological formations from which the raw materials are mined. Average concentrations of these constituents are listed in Table 2.1. The concentrations of each component in a given raw material might be higher or lower, depending on the source of the raw material.

2.2 The production of cement

Cement manufacturing consists of raw meal grinding, blending, pre-calcining, clinker burning, and cement grinding. A process flow diagram of the cement manufacturing process is shown in Figure 2.1. In short, limestone and other materials containing calcium, silicon, aluminum, and iron oxides are crushed and milled into a raw meal. This raw meal is blended (in blending silos) and then heated in the pre-heating system (700-900°C) to initiate the dissociations of carbonate to calcium oxide and carbon dioxide, which is called the calcining zone. A secondary fuel is fed into the preheating system to keep the temperature sufficiently high. After that, the temperature is increased to the range of 900 to 1,200°C. In this zone, calcium oxide reacts with silica dioxide to produce dicalcium silicate (Ca_2SiO_4, (C_2S)). Then, calcium oxide reacts with dicalcium silicate to produce tricalcium silicate (Ca_3SiO_5, (C_3S)). Tricalcium silicate occurs at the temperature range of 1,250 to 1,450°C. The meal then proceeds to the kiln for heating, which produces reactions between calcium oxide and other elements to form calcium silicates and aluminates at temperatures of up to 1450°C. Primary fuel is used to keep the temperature high enough in the burning zone for the chemical reaction to take place (Kaantee et al, 2000). After that, the temperature is decreased very quickly to prevent the decomposition of tricalcium silicate. During the cooling step, tricalcium aluminate ($Ca_3Al_2O_6$, (C_3A)) and tretacalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$, (C_4AF) is formed. The chemical reactions of each step are shown in the equation below. The reaction products leave the kiln as a nodular material called *clinker*. The nodules are approximately 0.1 to 0.75 inches (3 to 20 mm) in diameter (Taylor, 1990). Cement kiln dust is collected by an electrostatic precipitator (EP) and typically returned to the kiln as raw feed. The composition of the clinker, as well as the names and formulas of the clinker components are listed in Table 2.2. The clinker is then inter-ground with gypsum ($CaSO_4 \cdot 2H_2O$) of 2 to 3%, limestone, and/or ashes into a fine product called *cement* (Alsop, 1998).

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (2.1)$$

$$2CaO + SiO_2 \longrightarrow 2CaO \cdot SiO_2 \qquad (2.2)$$

$$CaO + 2CaO \cdot SiO_2 \longrightarrow 3CaO \cdot SiO_2 \qquad (2.3)$$

$$2CaO + CaO \cdot Al_2O_3 \longrightarrow 3CaO \cdot Al_2O_3 \qquad (2.4)$$

$$CaO + CaO \cdot Al_2O_3 + 2CaO \cdot Fe_2O_3 \longrightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \qquad (2.5)$$

Table 2.1: Concentrations (ppm) of metals and halogens present in the cement raw materials and in the earth's crust (Environmental Toxicology International Inc., 1992).

Constituent	Limestone	Clay/Shale	Earth's Crust
Metals			
Antimony	NDA[a]	NDA	1[b6]
Arsenic	0.2-12	13-23	5
Barium	NDA	NDA	250
Beryllium	0.5[b]	3	6
Cadmium	0.035-0.1	0.016-0.3	0.15
Chromium	1.2-16	90-109	200
Lead	0.4-13	13-22	16
Mercury	0.03	0.45	0.5
Nickel	1.5-7.5	67-71	80
Selenium	0.19	0.5	0.09
Silver	NDA	0.07	0.1
Thallium	0.05-0.5	0.7-1.6	0.6
Vanadium	10-80	98-170	150
Zinc	22-24	59-115	132
Halogens			
Bromine	5.9	1-58	1.6
Chlorine	50-240	15-450	314
Fluorine	100-940	300-990	300
Iodine	0.25-0.75	0.2-2.2	0.3

Remark: [a] NDA= no data available, [b] Estimated concentration

Table 2.2: Clinker composition of Portland cement (Environmental Toxicology International Inc., 1992).

Chemical name (Common name)	Chemical formula (Common notation)	Composition in Portland Clinker
Tricalcium silicate (alite)	Ca_3SiO_5 (C_3S)	50-70%
Dicalcium silicate (belite)	Ca_2SiO_4 (C_2S)	15-30%
Tricalcium aluminate	$Ca_3Al_2O_6$ (C_3A)	5-10%
Tetracalcium aluminoferrite	$Ca_4Al_2Fe_2O_{10}$ (C_4AF)	5-15%

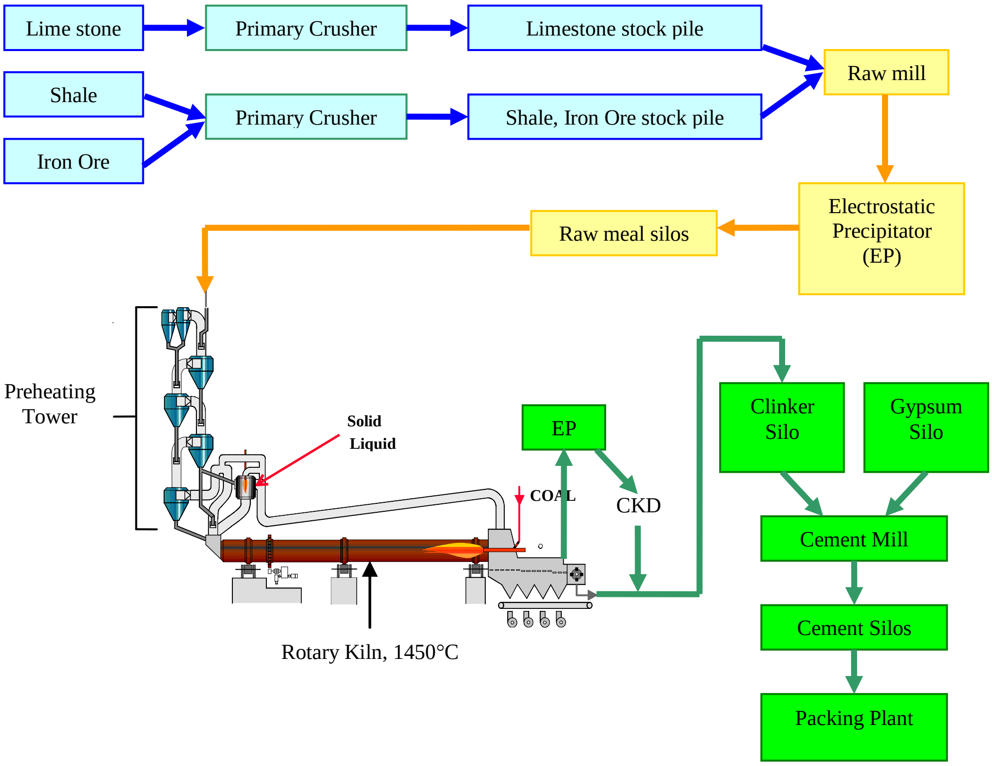


Figure 2.1: Process flow diagram of the cement manufacturing process (Holcim, 2006)

2.3 Energy and temperature in the rotary cement kiln

The majority of the heat energy is used to preheat the feed solids and convert the limestone to lime (calcinations) at the temperatures that are demonstrated in Figure 2.2. In the drying and preheating zone, the free and chemically bound water is evaporated and the temperature of the feed material is raised to 700 to 900°C, and in the calcining zone, the material reaches temperatures as high as 1200°C. The maintenance of the raw material temperature at about 1450 °C in the sintering zone is accomplished through an exothermic reaction. Having raised the temperature of the Portland cement clinker to 1450-1500°C in order to achieve the required level of combination, it is important to recover as much heat as possible and to return it to the process. To do this, the hot clinker is passed through a cooler. However, a high rate of clinker cooling between the temperature of the burning zone and about 1200°C is important if the best strength-giving properties are to be achieved. Microscopic examinations of clinkers which have been slowly cooled from 1450 to 1200°C often reveal a situation where the alite has affected a partial transformation into belite and free lime. The C_3A exhibits a tendency to crystallize from the flux in a form which is more reactive and which may lead to setting problems. There is also a danger with clinkers relatively high in magnesia that this can crystallize from the flux as periclase and lead to long-term unsoundness. The clinker coolers also need something like 3.0-3.5 kg of air to cool 1 kg of clinker (Hewlett, 1998).

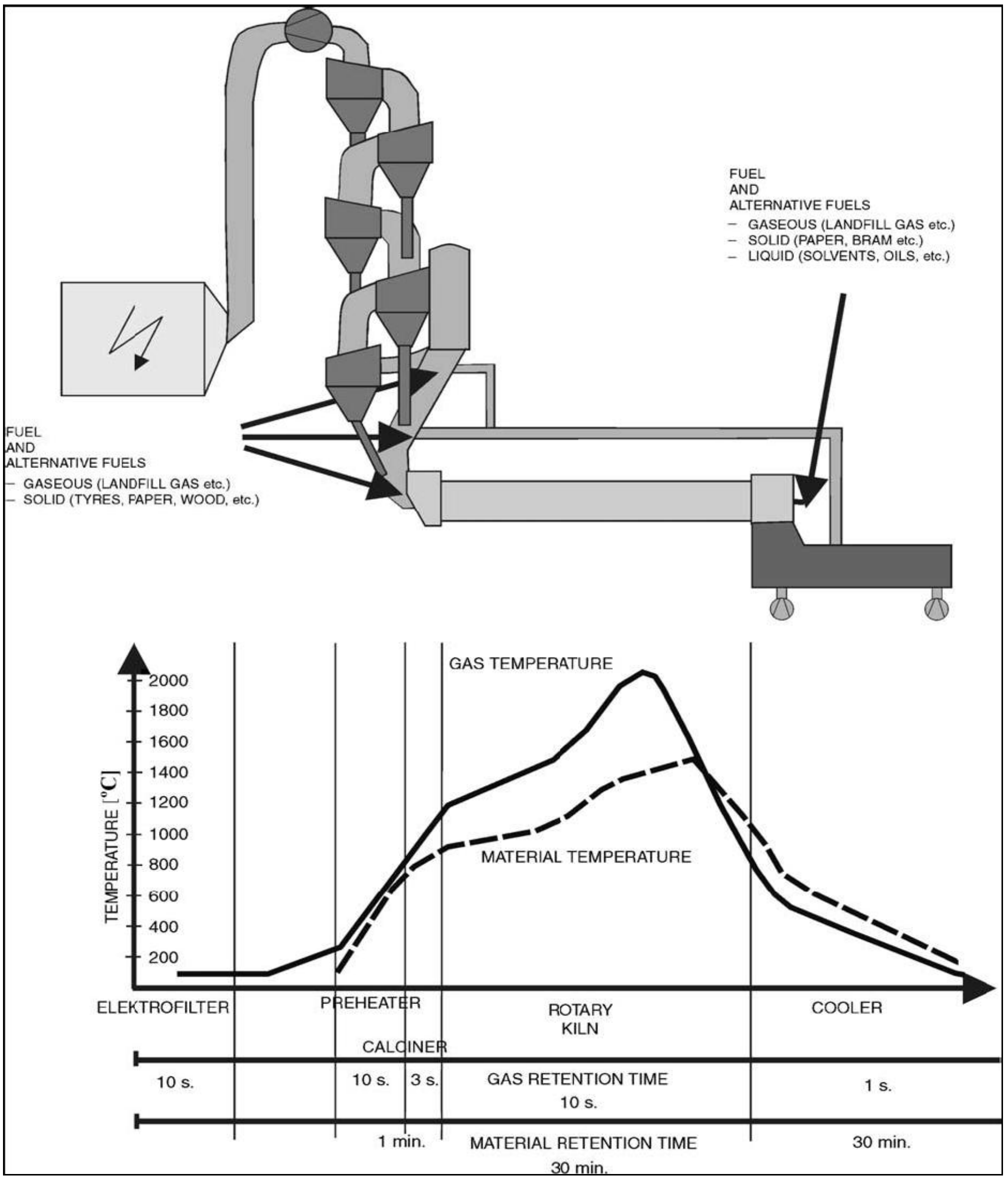


Figure 2.2: A diagram of the temperatures of gases and materials in a cement kiln (Mokrzycki et al., 2003)

Radiation of heat from the hot gases to the feed bed occurs only at the surface of the bed that is exposed to the gas. Thus the temperature of the bed is lowest in the center and highest on the surface (Peray, 1986). Heat transfers from the kiln wall on the feed. The flame radiates heat to the coating adhering to the kiln. Part of the heat then radiates to the bed, and part is transferred to the feed by conduction when the wall turns into the bed. Figure 2.3 shows that the wall temperature is lowest when it emerges from the bed and highest immediately before it comes into contact with the feed bed. The slower the kiln speed and the smaller the cross-sectional loading (feed) of the kiln, the larger will be the temperature difference between these two points. There is a temperature drop between the coating surface (CS) and the kiln shell (KS), the heat flowing in the direction indicated by the arrow as shown in Figure 2.4. (Heat always travels from a place or body of high temperature to a place of body of lower temperature). This heat transfer is governed to a great extent by the conductivity of the refractory and the coating.

Operating conditions are just as vital for coating formation; assume that a kiln will be operated from one extreme of temperature to the other, that is, a cold, a normal, and a badly overheated kiln as shown in Figure 2.5.

First, consider the cold kiln (Figure 2.5A). In this case almost no coating is formed. The coating surface temperature as well as the feed temperature is too low to produce the necessary amount of liquid matter that would promote coating formation. The condition in this example is commonly referred to by kiln operators as the kiln being in a “hole”. This example also supports the widely known fact that no new coating can be formed while the kiln is cold.

In the normal kiln (Figure 2.5B); enough liquid (24%) is present to form a coating. Temperature of the coating when it emerges from the feed bed, as well as when in contact with the feed, is below the solidifying temperature of the feed particles. The particles will adhere to the wall and solidify, and will continue to do so as long as the surface temperature of the coating remains below the solidifying temperature of 1315°C. Whenever the wall reaches this temperature no new coating will form. The coating is in equilibrium.

In the hot kiln (Figure 2.5C); because of the extremely high temperatures of the feed and the coating, too much liquid is formed. As all temperature is above the solidifying temperature, the coating transforms from a solid back to a liquid again. In such a condition, coating will come off, and the feed because of its high liquid content will “ball up.” Needless to say, this condition is extremely harmful to the kiln and to the refractory.

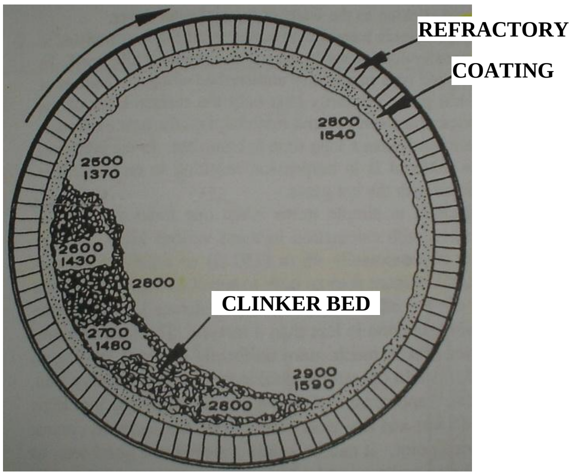


Figure 2.3: Wall temperature of the kiln in the burning zone (Peray, 1986).

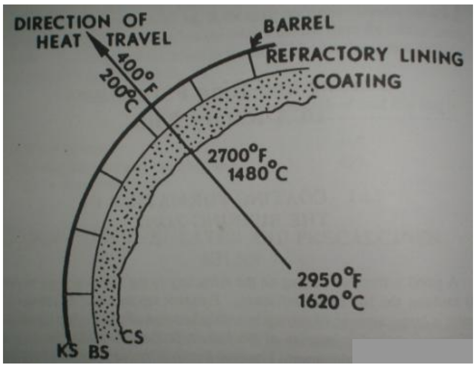
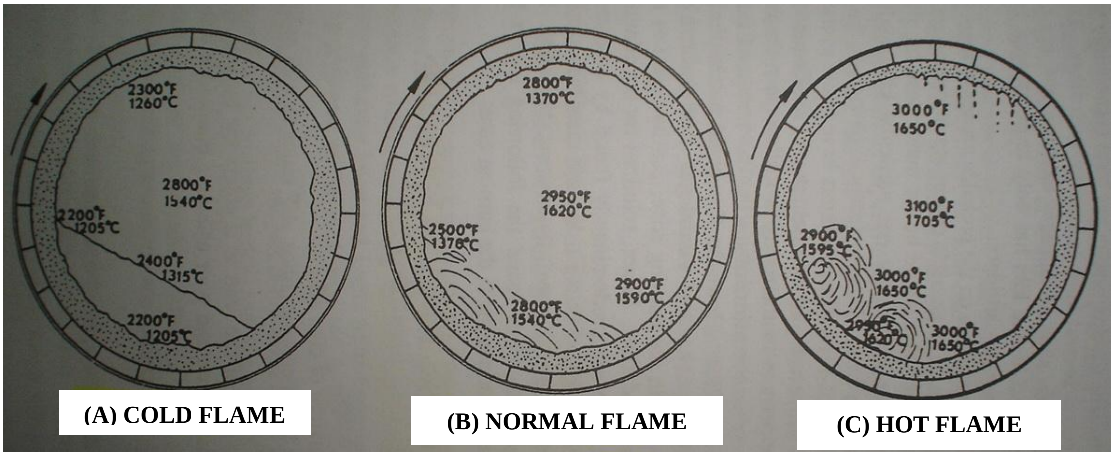


Figure 2.4: Heat, passing through the shell of the kiln (Peray, 1986).



(A) COLD FLAME

(B) NORMAL FLAME

(C) HOT FLAME

Figure 2.5: Coating and ring formations in a rotary kiln (Peray, 1986).

2.4 System chemistry in the kiln

Chemical reactions occur in the kiln, the temperature increases when going from the meal feed to the rotary kiln. The most important oxides that participate in the reaction are $CaCO_3$, SiO_2, Al_2O_3, and Fe_2O_3. Up to about 700°C, water is removed from the meal. In the preheating section (700-900°C), calcinations as well as the initial combination of alumina, ferric oxide, and silica with lime takes place. Between 900°C and 1200°C belite, C_2S ($2CaO*SiO_2$), forms. Above 1250°C, a liquid phase appears and this promotes the reaction between belite and free lime that forms alite, C_3S ($=3CaO*SiO_2$). During the cooling stage, the molten phase forms C_3A, tricalcium aluminate ($3CaO*AlO_3$), and if the cooling is slow the alite may dissolve back into the liquid phase and appear as secondary belite (Hewlett, 1998). Usually the reduction of clinker is done so that one type of clinker allows the plant to manufacture several well-defined types of cement that comply with the physical demands specified by cement standards.

The calculation of the potential composition of Portland cement is based on the word of R.H. Bogue and others, and is often referred to as “Bogue composition”. Bogue’s equations for the percentages of main compounds in cement are given below (Bernal et.al., 1952).

$$C_3S = 4.07(CaO)–7.60(SiO_2)–6.72(Al_2O_3)–1.43(Fe_2O_3)–2.85(SO_3) \quad (2.6)$$

$$C_2S = 2.87(SiO_2) – 0.75(3CaO{\cdot}SiO_2) \quad (2.7)$$

$$C_3A = 2.65(Al_2O_3) – 1.69(Fe_2O_3) \quad (2.8)$$

$$C_4AF = 3.04(Fe_2O_3) \quad (2.9)$$

Estimating the composition of cement is aided by more rapid methods of determining the elemental composition, such as X-ray fluorescence, X-ray diffraction spectrometer, atomic absorption, flame photometry, and electron probe micro-analysis. X-ray diffractometry is useful in the determination of free lime.

A number of factors enter into the composition of cement and, leaving on one side the minor constituents, they include the C_3S, C_3A, silica modulus (SM), lime saturation factor (LSF), free lime, SO_3, specific surface area, amount of material coarser than 32 or 45 µm, loss of ignition, and alkalis. The compound compositions of Portland cements containing no secondary materials and having an alumina/ferric oxide ratio equal to or more than 0.64 may be calculated from the oxide analyses as follows (Hewlett, 1998):

$$\% \text{ tricalcium silicate } (C_3S) = (4.071 \text{ x } \%CaO) - (7.700 \text{ x } \%SiO_2) - (6.718 \text{ x } \%Al_2O_3) - (1.430 \text{ x } \%Fe_2O_3) - (2.852 \text{ x } \%SO_3) \quad (2.10)$$

$$\% \text{ dicalcium silicate } (C_2S) = (2.867 \text{ x } \%SiO_2) - (0.7544 \text{ x } \%C_3S) \quad (2.11)$$

$$\% \text{ tricalcium aluminate } (C_3A) = (2.650 \text{ x } \% \ Al_2O_3) - (1.692 \text{ x } \%Fe_2O_3) \quad (2.12)$$

$$\% \text{ tetracalcium aluminoferrite } (C_4AF) = (3.043 \text{ x } \%Fe_2O_3) \quad (2.13)$$

The appropriate amount and form of calcium sulfate to a specific surface area (Blaine) of 300-350 m^2/kg, develops a 28-day strength (When tested using the method given in EN 196-1) of 50-65 N/mm^2. In addition to this, there are also constraints associated with the use of the clinker to prepare cements for special purposes where sulfate resistance, sea water resistance, low alkali release and high early strengths are required. The calculated calcium silicate content is compared with that measured by X-ray diffraction (XRD) there are some differences, as shown in Table 2.3 (Hewlett, 1998). And a material would require an oxide analysis which approximate to that given in Table 2.4 and 2.5. The remainder of the composition of the Portland cement clinker comprises compounds which are either necessary in order to achieve the required degree of combination in the course of thermal processing or are uneconomic to remove from the available raw materials. These include:

- 0-16 percent of tricalcium aluminate (C_3A)
- 1-17 percent of tetracalcium aluminoferrite (C_4AF)
- 0.5-6 percent of magnesia (MgO)
- 0.5-3 percent of alkali sulfates Na_2SO_4, K_2SO_4 and other compounds incorporating them
- 0.2-4 percent of uncombined calcium oxide (CaO-free)

2.5 Chemical composition in Portland cement

2.5.1 Tricalcium silicate (C_3S), which is called alite, is an important composition as it is responsible mainly for early strength development of mortar and concrete. C_3S is a highly hydraulic compound occurred in amounts of 50-90% in Portland cements. C_3S is formed above 1250°C by a reaction of C_2S and CaO and can be metastably obtained by rapid cooling of the mixtures. The crystalline structural model and photomicrograph of major components of clinker are given in Figure 2.6 (a) and 2.7, respectively. Alite is in polymorphic form by other ions, so high SO_3 contents even can suppress alite formation which otherwise can be partly avoided by the presence of fluorine ions (Welch and Gutt, 1959). A stabilization of polymorphs can be obtained by the incorporation of other ions in alite-lattice. For example, at $1500^{o}C$, up to 1.4 percent K_2O and Na_2O, and 1.2 percent of Li_2O can be incorporated in clinker. Up to 5% ZnO can be incorporated (Older, 1990), whereas 1.4% of Cr_2O_3 can be incorporated in clinker (Bensted and Barnes, 2002).

2.5.2 Dicalcium silicate (C_2S), which is called belite, mainly occurs in an amount of 10-40% in the clinker. C_2S is capable of incorporating larger amounts of foreign ions than C_3S. Activated C_2S can be obtained by rapid cooling, lattice distortions by solid solutions, crystal size, crystallochemical changes and chemical shift of bonding energies. The phase of γ- C_2S is known as 'dusting' due to an enormous volume change and due to the fact that it is barely hydraulic. β- C_2S can be obtained by quenching or doping; it usually occurs in cement. In Portland cement, belite originates from three different sources (Sorrentino, 1998). The structural model of C_2S is shown in Figure 2.6 (b).

2.5.3 Tricalcium aluminate (C_3A), which is called aluminite, the most abundant Al contained in Portland cement. Several polymorphs as a function of Na, Fe, and S content have been synthesized (Bensted and Barnes, 2002, and Mindess, Young, and Darwin 2003). C_3A crystallizes is a cubic form such as 0-1.9% Na_2O = cubic form, 1.9%-3.7% Na_2O = cubic + orthorhombic, 3.7%-4.6% Na_2O = orthorhombic, 4.6%-5.9% Na_2O = monoclinic, but it incorporates with alkalies (Na replace to Ca), and SiO_2, and changes to the orthorhombic and monoclinic forms. The ranges of the Na ion can change C_3A form as follow (Bensted and Barnes, 2002). C_3A is responsible for the workability of the mortar. The higher the C_3A content, the higher the plasticity of the mortar. This explains why raw material for plastic cements has a higher C_3A potential than typical cement. The C_3A has 6-8% of the clinker. Concrete containing cement high in C_3A is not as resistant to attack by sulfates in soil or water exposure as is concrete made with low C_3A cement. The structural model of C_3A is shown in Figure 2.6 (c).

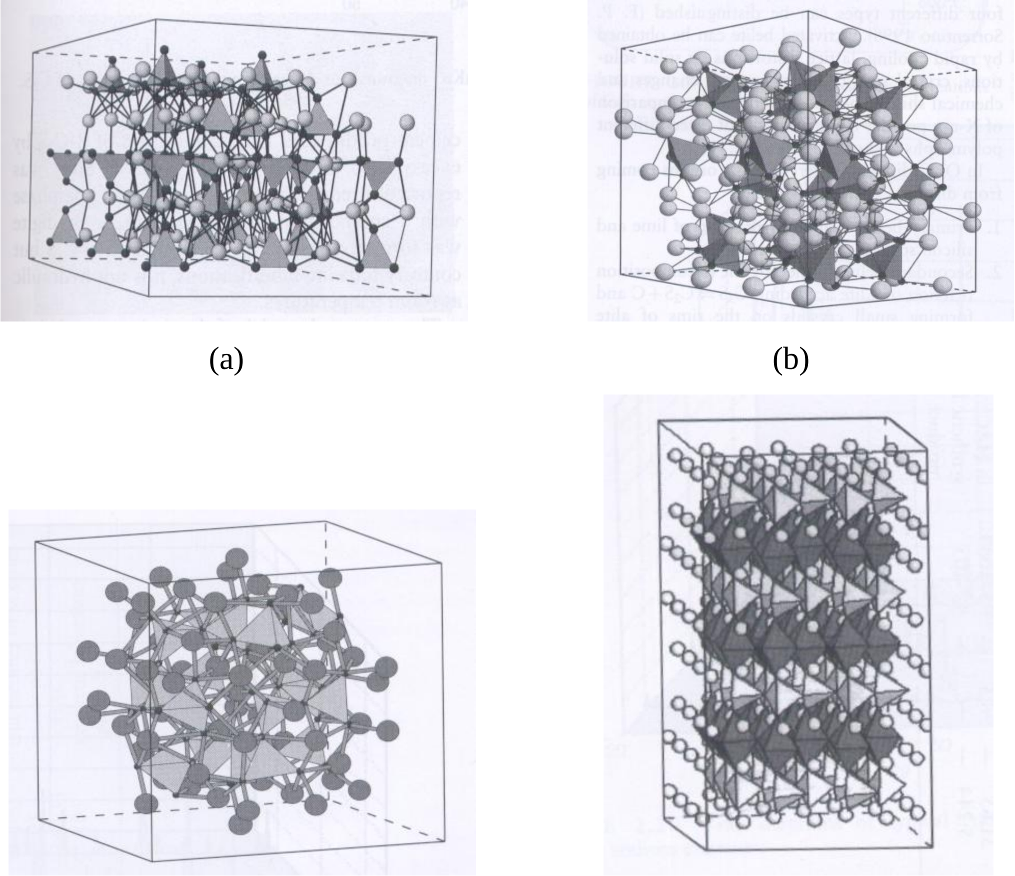
2.5.4 Tetracalcium aluminoferrite (C_4AF), which is called ferrite, governs the color of the cement. The higher the content of C_4AF in the clinker causes the darker the cement. In typical clinkers, the uptake of magnesium (Mg^{2+}), titanium (Ti^{4+}), and silicon (Si^{4+}) takes place. Fe dictates the burning condition. Reducing the condition can lead to the formation of Fe^{2+}. It leads to the increased formation of calcium aluminate and free lime. Fe^{2+} cannot be incorporated in the ferrate phase. Iron has the desirable property of acting as a fluxing agent in the kiln, facilitating formation of other compounds of the cement at somewhat lower temperature than would otherwise be possible. The structural model of C_4AF is shown in Figure 2.6 (d) (Bensted and Barnes, 2002; Brown, 1948).

Table 2.3: Analysed and calculated calcium silicate contents (percent)
(Hewlett, 1998).

Composition	Determined using XRD and microscopy	Determined using Bogue formulae based upon oxide analyses
C_3S (alite)	66-82	42-68
C_2S (belite)	2-32	10-36

Table 2.4: Ideal composition of raw material (percent) (Hewlett, 1998).

Component	Dry raw material	Clinker made from the dry raw material (assuming no coal ash absorption)
SiO_2	14.0	20.9
Al_2O_3	4.1	6.1
Fe_2O_3	1.6	2.3
CaO	43.2	64.5
Free lime	-	1.0
C_3S (Bogue)	-	55
C_2S (Bogue)	-	18
C_3A (Bogue)	-	12.2
C_3AF (Bogue)	-	7.0



(a) (b)

(c) (d)

Figure 2.6: Structure model of major components of clinker: (a) C_3S (b) C_2S (c) C_3A (d) C_4AF (Bensted and Barnes, 2002).

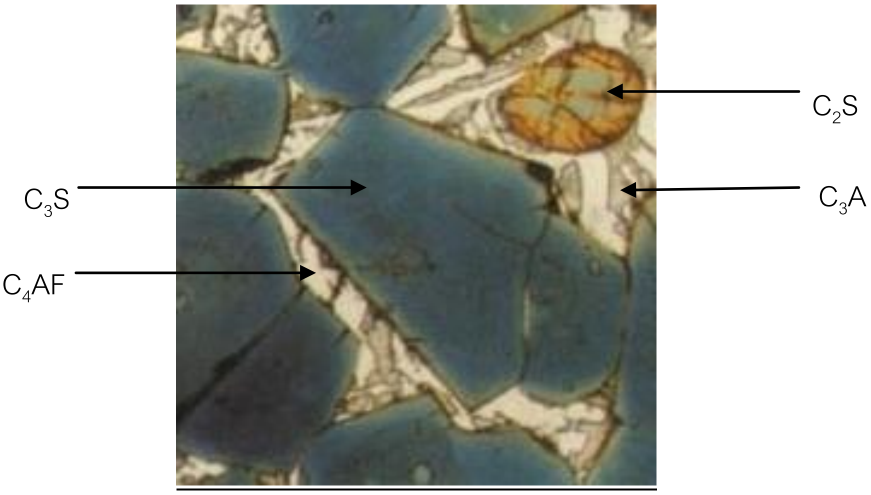


Figure 2.7: Photomicrograph of major components of clinker (0.11mm.): C_3S (blue), C_2S (orange), C_3A (grey), and C_4AF (white)

Table 2.5: Cement kiln feedstock based upon four components (percent) (Hewlett, 1998).

Component	Limestone	Shale	Sand	Iron oxide	Feedstock composition	Clinker made from the dry raw material (no coal ash absorption)
Dry material	73	22.5	4.2	0.3	-	-
used	1.4	37.9	95.0	2.7	13.6	20.3
SiO_2	0.5	16.5	1.4	6.6	4.2	6.2
Al_2O_3	0.2	5.1	1.3	84.0	1.6	2.4
Fe_2O_3	53.7	15.4	1.0	2.7	42.7	64.1
CaO	95.9	27.5	-	-	-	-
$CaCO_3$	-	-	-	-	-	1.0
Free lime	-	-	-	-	-	57
C_3S (Bogue)	-	-	-	-	-	15
C_2S (Bogue)	-	-	-	-	-	12.4
C_3A (Bogue)	-	-	-	-	-	7.3
C_4AF (Bogue)						

The other matter which has to be considered is the amount of flux at equation below which is present in the hottest part of the kiln-known in the industry as the 'burning zone'. This may be calculated for systems where the ratio of alumina to ferric oxide (A/F ratio) is above 1.38 and the amount of magnesia present is less than 2 percent, from the oxide analyses using the following formulae (Hewlett, 1998; Lea and Garston, 1935):

$$\text{Flux at } 1338°\text{C} = 6.1 \times \%\,Fe_2O_3 + \%MgO + \%\,K_2O + \%Na_2O \qquad (2.14)$$

$$\text{Flux at } 1400°\text{C} = 2.95 \times \%Al_2O_3 + 2.2 \times \%\,Fe_2O_3 + \%MgO + \%\,K_2O + \%Na_2O \qquad (2.15)$$

$$\text{Flux at } 1450°\text{C} = 3 \times \%Al_2O_3 + 2.25 \times \%\,Fe_2O_3 + \%MgO + \%\,K_2O + \%Na_2O \qquad (2.16)$$

Where the A/F ratio is less than 1.38 a modified formula is required for the flux at 1338°C;

$$\text{Flux at } 1338°\text{C} = 8.5 \times \%Al_2O_3 - 5.22 \times \%\,Fe_2O_3 + \%MgO + \%\,K_2O + \%Na_2O \qquad (2.17)$$

Flux levels less than 19 percent at 1400°C and 1450°C usually mean that the extent of the coating which builds up on the refractory lining of the kiln is minimal and that in consequence it may deteriorate more rapidly due to thermal damage.

It is not only the chemical composition of the main components of the feedstock which is important. The physical form plays an important part in both the quality of the product and the operation of the process. The raw materials come in various degrees of hardness and in the course of combination do not all achieve the same level of fineness. This is illustrated in Table 2.6. From these results, it will be seen from the very high silica ratio of the coarsest fraction that it would be very difficult to react in the limited time the material is exposed to the high temperature zone in the rotary kiln. The 45/90 µm fraction has a very high potential C_3S content which would make it difficult to combine. From their C_3A and C_4AF contents, both these fractions would have a low potential to provide flux. Microscopic examination revealed high free silica (sand) content in both of the coarser fractions.

Table 2.6: Size fractions of different raw materials (Hewlett, 1998).

Component	Fraction coarser than 90 µm	Fraction coarser than 45 µm but finer than 90 µm	Total kiln feedstock
SiO_2 (%)	20.0	15.4	13.9
Al_2O_3 (%)	1.3	1.5	3.3
Fe_2O_3 (%)	0.7	0.8	1.7
CaO (%)	43.5	45.3	43.8
Lime saturation factor	0.75	1.00	1.01
Silica modulus	10.0	6.7	2.8
Alumina modulus	1.9	1.9	1.9
Potential C_3S (%)	15	56	48
Potential C_2S (%)	46	2	4
Potential C_3A (%)	2.2	2.6	5.9
Potential C_4AF (%)	2.1	2.4	5.2

$$\text{Lime saturation factor (LSF)} = \frac{\%\ \text{CaO}}{(2.8\text{x}\%\text{SiO2} + 1.2\text{x}\%\text{Al2O3} + 0.65\text{x}\%\text{Fe2O3})} \qquad (2.18)$$

$$\text{Silica modulus (SM)} = \frac{\%SiO2}{(\%Al2O3 + \%Fe2O3)} \qquad (2.19)$$

$$\text{Alumina modulus (AM)} = \frac{\%\ Al_2O_3}{\%\ Fe_2O_3} \qquad (2.20)$$

This is illustrated by the quantitative effect that these factors have combined in the clinker as shown by the amount of free lime remaining after firing a given temperature (Hewlett, 1998).

$$\text{Percent free lime at 1400°C} = 0.31\ (LSF\text{-}100)+2.18(M_s\text{-}1.8) +0.73(Q45)+0.33(C125)+0.34(Aq) \qquad (2.21)$$

$$\text{Percent free lime at 1500°C} = 0.21\ (LSF\text{-}100)+1.59(M_s\text{-}1.9) +0.40(Q45)+0.22(C125)+0.08(Aq) \qquad (2.22)$$

Or when expressed in terms of the free lime achieved after firing at 1400°C;

$$\text{Percent free lime at 1500°C} = 0.54\ (\text{free lime at 1400°C}\text{-}1.7)+0.04(LSF\text{-}100) +0.41(M_s)+0.04(C125)-0.11(Aq) \qquad (2.23)$$

Where LSF = 100 (lime saturation factor);

M_s = silica modulus;

Q45 = percent quartz found in the material coarser than 45 microns;

C125 = percent residue on a 125 µm sieve;

Aq = non-quartz material coarser than 45 µm.

2.6 Hydration reaction in Portland cement

The hydration reaction is the reaction between water and Portland cement. Portland cement is mixed with sand gravel and water producing the synthetic rock that is called concrete. When water is added to cement, each of the compounds undergoes hydration and contributes to the final concrete product. Only the calcium silicates contribute to strength. Tricalcium silicate is responsible for most of the early strength (first 7 days) of the cement. Dicalcium silicate, which reacts more slowly, contributes only to the long term strength of the cement. The four principal hydration stages of Portland cement are described in Table 2.7 (Neville, 2003; Bensted and

Barnes, 2002; and Mindess, Young, and Darwin, 2003). In general, the rate of hydration occurs in on the order of C_3A > C_3S > C_4AF > C_2S. Reactions for even identical compounds may vary due to the following reason: 1) the fineness, 2) the cooling rate of clinker, and 3) impurities. Heat is produced by 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.

Table 2.7: The four principal hydration stages of Portland cement.

Processing stage	Chemical processes	Physical processes	Relevance to physical properties of concrete
First minutes (wetting and mixing)	Rapid dissolution of free lime, sulphate and aluminate phases; AFt immediately forms; Superficial hydration of C_3S occurs. Hemihydrate dissolves, but gypsum or syngenite can form	Large initial burst of heat, mainly from dissolution of aluminate phases, plus some from alite and CaO. (dissolution of alkali sulphates is endothermic)	Rapid formation of aluminate hydrates, plus gypsum and syngenite influence rheology and may also affect the subsequent microstructure.
Induction period (agitation, transport, placing and finishing)	Nucleation of "C-S-H(m)"; Rapid decrease in SiO_2 and Al_2O_3 to very low level; CH becomes supersaturated; SO_4^{2-} stay fairly stable	Low heat evolution rate; slow formation of early C-S-H and more AFt leads to continuous increase of viscosity (in absence of admixtures)	Continued formation of AFt and AFm phases can influence workability, but it is formation of C-S-H that usually leads to the onset of normal set.
Acceleration period (setting and early hardening)	Hydration of C_3S (to C-S-H and portlandite) accelerates and reaches maximum; CH supersaturation - decreases. SO_4^{2-} stay fairly stable	Rapid formation of hydrates lead to solidification and decrease in porosity; high rate of heat - evolution.	Change from plastic to rigid consistency (initial and final set); early strength development.
Post-acceleration period (demoulding; continued hardening)	Decelerating rate of formation of C-S-H and portlandite from- both C_3S and C_2S; OH increase but low level of SO_4^{2-}; renewed hydration of aluminates to give mainly AFm phase, AFt may redissolve and/or recrystallize.	Decrease in rate of heat evolution. Continuous decreasing in porosity particle-to-particle and paste-to-aggregate bond formation.	Continuous strength increase due to decreasing porosity, but at an ever-diminishing rate. Decrease in creep capacity. Hydration continuous for years if water is available. Paste will shrink due to drying

2.7 Alternative fuels and raw materials

There are several types of industrial waste. Examples of solid waste are as follows: the wastewater sludge from a bio-chemical treatment system, chemically-contaminated soil or contaminated materials (e.g., fabric scrap, paper scrap, and plastics), ash from power plants, and rice chaff. Liquid waste includes alkaline solvents, used engine oil, high-organic wastewater, wastewater from a chemical rinsing and cooling process, etc. These wastes require efficient, low-cost treatment. Incineration by a cement kiln is an interesting alternative nowadays as shown in Figure 2.8. The heavy metal and transition metal contents of industrial clinkers produced by the burning of wastes can be below the detection limit of conventional analysis methods; V (as NH_4VO_3), Zn (as ZnO) and Pb (as $Pb(NO_3)_2$) are examples of these types of metals. Relatively large amounts of V are naturally present in coal and petcoke, the major fuels currently utilized in Brazilian kilns (Andrade et al., 2003). Zn is present as a minor element in tires, which is a non-hazardous waste extensively used as an alternative fuel source in the cement industry worldwide. Pb commonly occurs as a trace element in raw material, fuels, and industrial waste and shows a relatively higher volatility in comparison to other trace elements.

Although a metal compound is changed in the combustion process, a metal, like any element, is not destroyed in a combustion device. Accordingly, metals will be present in the emissions, the CKD, or the clinker. In February 1991, the U.S. EPA finalized the Boilers and Industrial Furnaces (BIF) rule, which applies additional requirements to the actual burning of hazardous waste in cement kilns as well as other boilers and industrial furnaces. The BIF rule requires that a facility demonstrate a 99.99% destruction and removal efficiency (DRE) for principal organic hazardous constituents (POHCs) in the waste stream. A DRE of 99.99% means that out of 1 ton put into the system, less than 4 ounces are actually emitted in the stack gas. Achieving this level of DRE “will ensure that constituents in the waste are not emitted at levels that could pose significant risks” (U.S. EPA, 1991). The BIF rule sets emission standards for 10 metals, antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, lead, mercury, silver, and thallium, because of their potential for adverse effects to human health and the environment. These metals are classified as either carcinogenic or noncarcinogenic, as shown in Table 2.8.

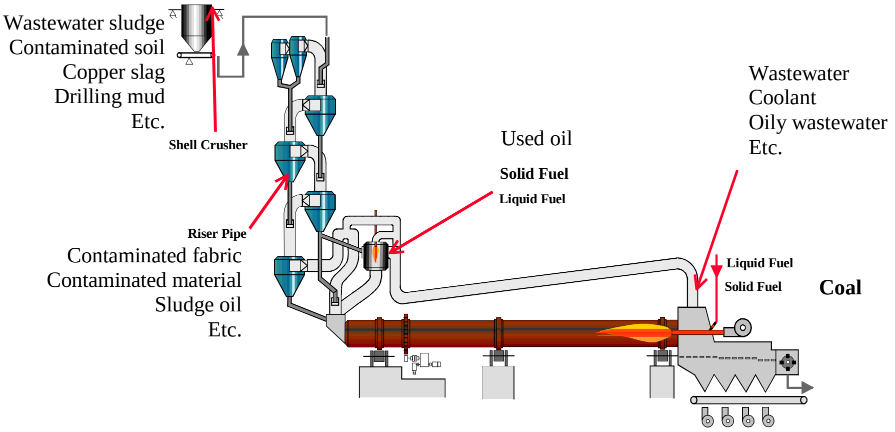


Figure 2.8: Alternative fuels and raw materials (AFR) injection locations in the cement manufacturing process (Holcim, 2006)

Table 2.8: Classification of carcinogenic metals and noncarcinogenic metals.

Carcinogenic metals	Noncarcinogenic metals
Arsenic (As), Beryllium (Be), Cadmium (Cd), and Hexavalent chromium (Cr^{+6})	Antimony (Sb), Barium (Ba), Lead (Pb), Mercury (Hg), Silver (Ag), and Thallium (Tl)

The Combustion Research Institute (CRI), a division of Environmental Toxicology International, has established a database to evaluate potential differences in metal emissions due to the burning of hazardous waste. The comparison of metal emission from a cement kiln shown in Table 2.9 demonstrates that the averages and ranges of metal emissions for cement kilns burning only conventional fuel appear to be similar to those of cement kilns replacing a portion of their conventional fuel with hazardous waste. In fact, the average emissions were lower for seven metals when a portion of the conventional fuel was replaced with hazardous waste.

Table 2.9: Comparison of metal emissions (mg/sec) from cement kilns (CKs) (Environmental Toxicology International Inc., 1992).

Metal	CKs Burning Conventional Fuel				CKs Burning Hazardous Waste Fuel			
	Avg	SD	Min	Max	Avg	SD	Min	Max
Antimony	0.685	1.58	<0.0100	5.76	0.808	1.78	<0.0100	5.08
Arsenic	0.991	1.65	<0.00736	5.70	0.592	0.890	<0.00723	2.80
Barium	10.7	37.7	0.0354	166	19.9	47.3	0.0218	144.76
Beryllium	0.0438	0.108	<0.000500	<0.369	0.0452	0.110	<0.000499	<0.326
Cadmium	0.344	0.376	<0.0220	1.29	0.309	0.317	<0.0218	1.34
Chromium	20.6	58.5	<0.0100	264	12.5	52.4	<0.0100	299.1
Lead	1.95	2.37	0.0527	12.0	5.83	10.4	0.0210	50.8
Mercury	0.984	2.39	0.0537	10.7	2.14	2.96	0.132	9.84
Nickel	17.3	40.1	<0.0663	138	11.0	34.5	0.0696	171.4
Selenium	0.0719	0.0678	<0.00736	0.260	0.0455	0.0684	0.00029	<0.195
Silver	0.555	1.04	<0.0220	3.96	0.886	2.26	<0.0217	7.94
Thallium	1.40	1.95	<0.00736	5.77	0.806	1.78	<0.00723	5.08
Vanadium	0.338	0.221	<0.0886	<0.620	0.359	0.245	<0.0868	0.62
Zinc	2.97	2.51	0.334	7.80	1.53	1.58	0.147	6.48

Note: Data reported at less than the detection limit were assumed to be present at the detection limits in order to calculate the averages (Avg) and standard deviations (Std Dev). This procedure will overestimate the actual concentrations present.

The CRI database has been designed to evaluate the potential differences in metal concentrations of CKD and clinker due to the burning of hazardous waste in cement kilns. The available compiled data summarized in Table 2.10 show that the average metal concentrations in CKD for cement kilns that burn only conventional fuel do not differ substantially from the average metal concentrations in CKD for cement kilns that burn hazardous waste as fuel. In addition, the ranges of metal concentrations are not substantially different (Environmental Toxicology International Inc., 1992). A comparison of the metal concentrations (ppm) in clinker is shown in Table 2.11. The information presented in this table should be reviewed with caution because it represents only a limited number of test results. The average metal concentrations in clinker produced from cement kilns burning hazardous waste do not appear to differ substantially from the average metal concentrations in clinker generated from kilns burning only conventional fuel. The ranges also appear to be approximately equivalent.

Table 2.10: Comparison of metal concentrations (ppm) in CKD
(Environmental Toxicology International Inc., 1992).

Metal	CKs Burning Conventional Fuel				CKs Burning Hazardous Waste Fuel			
	Avg	SD	Min	Max	Avg	SD	Min	Max
Antimony	16	36	<1	105	15	38	<1	124
Arsenic	25	12	12.8	44.1	23	19	1.67	65
Barium	161	49.8	119	271	137	57.4	56.1	279
Beryllium	1.0	0.96	<0.5	2.68	1.6	0.88	<1	3.93
Cadmium	5.6	7.3	1.9	25	9.3	11	<0.5	40
Chromium	53	18	27.3	84.4	50	29	17.6	113
Lead	83.1	41.0	23.2	144	277	228	66.9	788
Mercury	0.4	0.6	0.0369	<2	0.4	0.8	0.0218	3
Nickel	40	7.7	26	50.5	22	11	6.27	47.1
Selenium	9.4	4.6	3.48	16.8	15	16	<0.5	39.1
Silver	6.0	7.5	<1	25	2.5	3.4	<1	10
Thallium	10.5	25.1	0.594	67.5	7.8	19	<1	60.5
Vanadium	127	35.5	56.5	167	63.0	33.7	10.1	101
Zinc	149	84.6	68.3	197	150	52.5	96.3	241

Note: Data reported at less than the detection limit were assumed to be present at the detection limits in order to calculate the averages (Avg) and standard deviations (Std Dev). This procedure will overestimate the actual concentrations present.

Table 2.11: Comparison of metal concentrations (ppm) in clinker
(Environmental Toxicology International Inc., 1992).

Metal	CKs Burning Conventional Fuel				CKs Burning Hazardous Waste Fuel			
	Avg	Std Dev	Min	Max	Avg	Std Dev	Min	Max
Antimony	1.5	0.44	<1	2.18	3.29	1.76	1.91	6.435
Arsenic	11.2	2.55	7.91	14.9	25	22	2.12	62.5
Barium	144	15.6	130	168	139	42.9	76.5	194
Beryllium	0.5	0	<0.5	<0.5	1.6	0.76	<1	3.18
Cadmium	3	0	<3	<3	0.7	0.2	<0.5	<1
Chromium					7.1	38.6	43.8	128
Lead	6.7	4.7	<1	14.3	17	42	<1	163
Mercury	0.2	0	<0.2	<0.2	0.2	0	<0.2	<0.2
Nickel					49.6	7.57	40.4	56.3
Selenium	0.6	0	<0.6	<0.6	9.1	12	<0.5	27.5
Silver	3	0	<3	<3	1.4	0.67	<1	2.49
Thallium	0.5	0	<0.5	<0.5	1	0	<1	<1
Vanadium	156	19.5	131	180	82.3	23.2	46.7	127
Zinc	23	17	4.44	50.3	64.9	34.2	13.55	113.7

Note: Data reported at less than the detection limit were assumed to be present at the detection limits in order to calculate the averages (Avg) and standard deviations (Std Dev). This procedure will overestimate the actual concentrations present

2.7.1 Heavy metals in cement: chromium, nickel, copper and zinc

2.7.1.1 Chromium

Chromium is a heavy metal that can be found in nature such as in rocks, soil, and plants. In cement industries, chromium is found in limestone, clay, char, and oil which are the fuel sources in production process (Sprung, 1985). Hazardous waste co-incineration in cement kilns uses waste as fuel or as raw material in partial substitution for natural materials. The use of bauxite as a source of alumina may increase concentration of chromium on the final product (Barros, 2004). Waste such as galvanic sludge and electroplating sludge can be used in the co-incineration (Denise et.al., 2000). Chromium has been found in industrial hazardous waste in the following concentration: 737 mg/l in burnt used oil (Trezza and Scian, 2000). Chromium cannot evaporate but it can appear in air in form of particle. In nature, it is found in three forms: metal ore, trivalent chromium (Cr III), and hexavalent chromium (Cr VI). Chemical properties of chromium are as shown in Table 2.12 (Vincoli, 1997). It is poisonous to humans when ingested --producing gastrointestinal effect--and inhaled. In general, Cr (VI) is more toxic than Cr (III) because its oxidizing potential is high and it easily penetrates biological membranes causing diseases such as skin eczema. The lethal dose of poisonous Cr (VI) is about one half of a teaspoon of material. The World Health Organization recommended a maximum allowable concentration in drinking water for Cr (VI) is 0.05 mg/l (Diane et al, 1992). In the hydration of cement, chromium can incorporate in ettringite. At pH 11-13, the sediment of $Cr(OH)_3$ was found and solution is Cr(VI). At pH 9-13, Cr(III) and Cr(VI) are incorporated into ettlringite and contain in calcium sulphoaluminate hydrate(Aft and AFm phase); in addition to, at pH lower than 3, Cr exists as $CrOH^{2+}$. (Gouger et.al.,1996).

Table 2.12: Chemical properties of chromium.

Atomic weight	51.996
Melting point	1,857°C
Boiling point	2,672°C
Density	7.14 g/cm^3

2.7.1.2 Nickel

Nickel is a heavy metal that can be found in the nature such as in soil and volcanoes. Pure nickel is hard, and silver-white in color. Nickel can be combined with other metals with other metals such as iron or copper to form of alloys. Nickel is carcinogenic to humans and animals; it can be ingested and inhaled as a powder or dust. Skin contact with the dusts of nickel may result in scratching and scarring. Ni is extremely toxic when its form in $Ni(CO)_4$ and which is more toxic than CO. Exposure to nickel and soluble compounds should not exceed 0.05 mg/cm^3 in a 40-hour work week (Kasprzak, 2003). In cement industries, the main sources of nickel in production Portland cement are limestone, clay, coal, oil, and coke (Sprung, 1985). Waste such as galvanic sludge and electroplating sludge were disposed in cement process. These wastes are one of the main sources of nickel (Ract et.al., 2003). Nickel has been found in industrial hazardous waste or sludge at the following concentration; 1.22% in galvanic sludge from electroplating factory, and 62,400 mg/l in sludge from a metal plate factory. In the burning process, 97% of Ni incorporated into the clinker (Barros, 2004). NiO is usually found in the ferrite but can present in the alite or belite. Concentration of NiO from 0.5% to 1% was incorporated in the alite (Barros, 2004).

In the hydration of cement at the pH of 9-12, nickel is in the form of $Ni(OH)_2$ and stable. In a CSH product, $Ni(OH)_2$ is incorporated at pH lower than 8, and also nickel leaches rapidly and in the form of Ni^{2+} (Gougar et.al.,1996). Chemical properties of nickel are as shown in Table 2.13.

Table 2.13: Chemical properties of nickel.

Atomic weight	58.71
Melting point	1,455°C
Boiling point	2,730°C
Density	8.9 g/cm^3

2.7.1.3 Copper

Since Cu is a heavy metal which is an element broadly dispersed in nature, and can be found in industrial waste such as wastewater sludge, galvanic sludges, copper slag etc. In process of cement raw mixes is containing Cu compounds and CuO can incorporated in the mineralogical phases of the clinker and its influence on the burnability and the sintering process of the cement raw mix (Kakali et.al.,1996). Cu is harmful if swallowed and inhaled. Cu and Ni are metals found in galvanic sludges; these sludges are considered hazardous due to their heavy metal content. The additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.%Cu and 1.2 wt.% Ni to clinker raw-material do not affect the clinkering reactions and that these metals are totally incorporated into the clinker (Ract et.al., 2003). Chemical properties of copper are as shown in Table 2.14.

Table 2.14: Chemical properties of copper.

Atomic weight	63.546
Melting point	1,084.62°C
Boiling point	2,562°C
Density	8.96 g/cm^3

2.7.1.4 Zinc

Zinc is an element that is usually found in earth's crust. In nature, zinc is in the form of sulfite, oxide, or carbonate. Zinc is a white metal and used in alloy, electroplating, metal spraying, and production of car part etc. Zinc has low toxicity condition, but when it changes to its salt form, it becomes highly toxic. The primary source of toxic zinc comes from the inhalation of zinc dust. The ingestion of zinc is not considered to be a toxic problem because zinc is poorly absorbed into the digestive tract. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. In the cement industries, zinc has been found in hazardous waste at the following concentration: 114,483 mg/l in burning used oil and 227,000mg/l in sludge from metal plate factories. (Trezza and Scian, 2000). Zinc is present as a minor element in tires (Andrade et.al., 2002). Zn delays the setting of clinker. In the hydration reaction of cement, at the pH of 8-12, zinc is in form of ZnO or $Zn(OH)_2$. When the concentration of ZnO is higher than 3 mg/l, ZnO is precipitated in the cement phase. ZnO can improve the burning behavior and lower the temperature. The phase formation with CaO is developed by the addition of ZnO. Through its combustion with sulphate and fluorides, the burning temperature can be lowered to 1050^{o}C. Up to 4.7 % of zinc can stabilize different polytypes of C_3S (Odler, 1990). Other phase with Zn was described-Ca_2ZnSiO_5 and different calcium aluminum zinc oxides are other phases that have been found with Zn. $ZnCO_3$ appears at pH 7-8. Chemical properties of zinc are as shown in Table 2.15.

Table 2.15: Chemical properties of zinc.

Atomic weight	65.37
Melting point	419°C
Boiling point	907°C
Density	7.14 g/cm^3

Heavy metal contamination can lead to adverse effects to on human health and the environment. So, many countries have designed the standards for limiting of heavy metals from alternative fuels and wastes that are used in cement plants. The table 5 lists the standard limit of several countries (Holcim, 2006). In Thailand, heavy metals concentrations in cement have been investigated every month. Concentrations of heavy metals in cement from the SCCC follow the New Holcim guideline in for the year 2007. Table 17 and Table 18 reported on the heavy metals in cement from the market in May 2007. The report of the maximum concentration of heavy metals in waste was set by SCCC as shown in Table 19.

Table 2.16: Limit values set by authorities for cement plants individual permits.

Parameter	unit	Spain	Belgium	France	Switzerland
Cr	mg/kg	-	1000	-	100
Ni	mg/kg	-	1000	-	100
Zn	mg/kg	-	5000	-	400
Hg	mg/kg	10	5	10	0.8
Cd	mg/kg	100	70	-	0.5
Cu	mg/kg	-	-	-	100
Sum of Sb + As + Co+ Ni+ Pb+ Sn+ V +Cr	mg/kg	0.5 %	1000	2500	-

Table 2.17: Concentration of heavy metals in clinker from the SCCC in May, 2007.

Clinker	Heavy metal(ppm)			
	Cr	Cu	Ni	Zn
New Holcim[c] Guild line 2007	19-270	4-280	10-101	13-370
Median	53	113	27	61
Proposed new S-QA-012 [d]	<150	<200	<80	<300
CL1	123	128	53	221
CL2	115	113	68	212
CL3	Shut down			
CL4	105	132	51	174
CL5	141	204[e]	52	270
CL6	124	208 [e]	52	271

[c] Information from Dr. Yves Zimmermann

[d], As recommend by Dr. Yves Zimmermann

[e] off proposed new S-QA-012 spec

Table 2.18: Heavy metal in cement market in May 2007.

Brand (continuous monitoring)	Heavy metal (ppm)				
	Cr	Cu	Ni	Zn	V
Elephant	101	282	65	816	0
Insee petch (plant3) [f]	143	180	48	260	0
Ratchasri Dang	165	280	65	362	0
TPI M299	199	224	68	715	0
Mountain	111	44	52	39	0

[f] from 2 samples

Table 2.19: Maximum concentration of heavy metal in waste was set by SCCC (Siam City Cement Public Co., Ltd.).

Heavy metals	Limits concentration (ppm)
Cr	5,000
Ni	1,000
Zn	10,000

2.8 Literature Review

The burning of industrial waste in cement kilns has an increasing environmental importance, brought about by the incorporation of potentially hazardous elements into the clinker crystalline phases and the partial substitution of primary fuel and raw materials. Andrade et al. found that clinkers were synthesized with the addition of V, Zn, and Pb to a standard raw meal, from which a control clinker was obtained for comparison. The three metals were chosen as they are present in the alternative fuel petcoke (i.e., V) and in industrial wastes (i.e., Zn and Pb), which are commonly burned in cement kilns. The electron microprobe and scanning electron microscope analysis revealed the preferential partition of these metals among the clinker's crystalline phases. It was observed that V has shown a preferential partition towards C_2S. Zn appears in higher amounts in periclase, and C_3S has higher Zn contents than C_2S. Pb concentrates in minute spherules and partitions toward C_3S in small amounts (Andrade et al., 2003). This study does not include other heavy metals such as As, Ba, Cr, Cd, Cu, Hg, Ni, Se, Sb, and Tl.

Stephan et al. (1999a) found that the influence of high intakes of Cr, Ni, and Zn on the burning process had affect to the formation of clinker phases. Three different raw meals were used and were burned with the metal oxides in four concentrations that varied from 200 to 25000 ppm. The resulting clinker was analyzed for its content of free lime, and X-ray diffraction analysis was performed. Some of the clinker material was crushed and polished, and quantitative point counting was performed to provide the content of the different clinker phases. These samples were also analyzed by a scanning electron microscope connected with an energy-dispersive X-ray-spectrometer to detect the composition of the clinker phase. The results showed that only very high intakes of heavy metals have measurable effects on the formation and composition of clinker.

Stephan et al. (1999b) presented the results of the hydration of cements with high intakes of Cr, Ni, and Zn. The cements were produced from clinkers that were doped with 200 to 25000 ppm of heavy metals. Differential scanning calorimetry was utilized to analyze the rate of heat generation in the cements in the first 2 days.. The hydration products were investigated by scanning electron microscopy combined with an energy-dispersive X-ray spectrometer and also by X-ray powder diffraction. The initial settings of some samples were tested, as well as compressive strength. The results showed that heavy metals only have an influence on the hydration properties of cements when their dosages are much higher than they are in ordinary Portland cement.

Polat et al. (2004) conducted a research on cement kiln dust, raw materials, and cement samples collected from a coal-fired cement factory, namely the Askale Cement Factory in Erzurum, Turkey. The samples were characterized with the standard addition method using energy-dispersive X-ray fluorescence techniques. An annular 100 mCi ^{241}Am radioactive source emitting 59.5 keV photon and annular 50 mCi ^{55}Fe radioactive sources emitting 5.96 keV photo were used for excitation. Samples were prepared from powder sifted by a 300-mesh sieve. The characteristic K X-rays of the different elements were detected with a Si (Li) detector. The results showed that Ca, Fe, and Sr were present in high concentrations in the CKD, cement (C), and raw materials (RM) of the Askale Cement Factory and there were no harmful elements, such as Pb, As, Bi, and Cd, which may damage the environment, in the CKD of the Askale Cement Factory.

Ract, Espinosa, and Tenorio (2003) showed that galvanic sludge could be considered hazardous due to its heavy metal contents of Cu and Ni. The main objective of this work was to determine the incorporation amounts of Cu and Ni in Portland clinker when a galvanic sludge containing these metals was added to the clinker raw-material. The influence of this addition on the clinkering reactions was evaluated as well as the possibility of co-incinerating galvanic sludge containing Cu and Ni in rotary cement kilns. This study also characterized the galvanic sludge. Samples were prepared with additions of 0.25 to 5 wt.% of a galvanic sludge to an industrial clinker raw-material. The clinkering process was simulated in a laboratory device. The following techniques were applied to characterize the raw materials and the products of the tests: chemical analysis, differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Leaching tests were performed in the produced clinker samples in order to verify the incorporation of the studied metals in the clinker structure. The results led to the conclusion that additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.% Cu and 1.2 wt.% Ni to clinker raw materials do not affect the clinkering reactions and that these metals are totally incorporated into the clinker.

Dalton et al. (2004) studied hundreds of millions of cubic meters of contaminated sediments that were dredged from US harbors and waterways annually for the maintenance of navigation or environmental remediation, or both. In recent years, inexpensive ocean dumping has been largely eliminated as a disposal alternative causing a crisis in the management of sediment. This paper presented a new beneficial alternative for using contaminated dredged material, which is the use of dredged material as a feedstock in the conventional manufacturing of Portland cement. The paper demonstrated the efficacy of the process at the bench and pilot scales, and presented a summary of the practical and economic considerations. A bench scale manufacturing was carried out with feedstock mixtures containing 1–12% dredged material from the New York/New Jersey (NY/NJ) harbor. The clinkers were quantitatively analyzed using X-ray powder diffraction and the differences in phase concentrations were observed in the clinker samples manufactured with dredged material (decreased alite and increased belite) suggesting that additional burn time was needed to account for the quartz present in the sediments. The free chloride concentrations in the clinker samples were below the ACI limits for cement used for reinforcing steel; however, the chloride in the dredged material remained a manufacturing concern and was expected to increase annual maintenance costs. A pilot-scale manufacturing project was carried out in a batch rotary kiln. X-ray diffraction analysis and ASTM tests for strength, soundness, and setting time suggested that with better optimized burning conditions, dredged material can be successfully incorporated into full scale manufacturing processes.

Richaud, Herod, and Kandiyoti (2004) examined four coal samples and three biomass samples had been ashed by low-temperature (LTA) and high-temperature (HTA) methods and a range of trace elements were measured in the coals, biomass, and ash samples. The digestion of solids was performed by both wet ashing and by microwave digestion; an examination of the resulting solutions was performed by inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry for certain elements. Hg was estimated by a spectrometric method. The trace elements examined were Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Mo, Cd, Sb, Ba, Pb, and Hg. Changes in concentrations in the LTA and HTA were compared with the raw materials that were observed. During LTA, Se and Hg were partially lost while Ba became more insoluble in nitric acid, indicating a change to Ba sulfate. The behaviour of trace elements in the coals on conversion to HTAs had been established in an earlier work and followed the expected trends, with Se, Hg, As, Cd, Pb, Zn being at least partially volatile. Trace element concentrations were generally greater in the coals than in the biomass samples, except for Mn, Cu, and Zn which were more concentrated in the biomass samples.

The stabilisation/solidification (S/S) process is a recognized technology used for the treatment of various hazardous wastes. Cement and pozzolanic materials such as pulverised fly ash (PFA) and blast furnace slag are usually used to bind various wastes into a stabilized solid form. Li X. D. et al. present a five-step sequential chemical extraction (SCE) procedure, which they employed to investigate the binding mechanisms and chemical partitioning of zinc in cement-based stabilised waste materials. After each step of SCE, a scanning electronic microscope with energy dispersive spectrometer (SEM/EDS) and X-ray diffraction (XRD) were used to assess the microstructural and chemical changes of the waste materials. The results showed that the leaching of Zn from the cement-based stabilised waste mainly took place at the second and the third extraction steps at pH 5.0 and 2.0, respectively. The addition of pulverised fly ash (PFA) increased the leachability of Zn at the second extraction step. The SCE results also indicated the hydration of cement was greatly retarded by the incorporation of zinc waste. The SEM and XRD analysis of the samples after each extraction step demonstrated that the zinc leached at the second extraction step was partially due to the dissolution of the new crystalline phase (ZnO) in the waste materials. Since large amounts of zinc were leached out only at the third extraction step at pH 2.0, these stablised waste materials may be relatively stable under a normal disposal environment (Li et al, 2001).

The use of industrial wastes as an alternative fuel in the cement industry is a practical reality in several countries because wastes are removed and economic incomes are obtained preserving non-renewable energy resources. The effect of the addition of small amounts of ashes from the pyrolysis of used car oil in the clinkering process of Portland cement was studied. The study simulated the burning process in an industrial furnace that uses up to 30% of this kind of waste fuel. The different behaviours of the clinker obtained (clinkering, milling, phases, hydration, etc.) were discussed and these behaviours were compared with those of a clinker obtained without additions. The residues of metals and metallic oxides incorporated to the clinker during the clinkering process through an alternative fuel (used oils from cars) do not seem to detrimentally alter the characteristics of the material (Trezza and Scian, 2000).

The crystal chemistry of the phases was found in cements by Prodjosantoso and Kennedy (2003) They have explored the solubility of Mg, Cd, Pb, and Ba in $Ca_3Al_2O_6$ using a combination of electron microscopy, X-ray microanalysis, and powder X-ray diffraction methods. The compounds formed when the divalent cations Mg^{2+}, Cd^{2+}, Ba^{2+}, and Pb^{2+} are present during the preparation of $Ca_3Al_2O_6$. The smaller Mg cations are found to partially substitute for Ca^{2+}, and structural refinements show that Mg preferentially occupies the smaller six-coordinate sites in $Ca_{3\_x}Mg_xAl_2O_6$. When Ba is present, it preferentially occupies the larger eight- and nine-coordinate sites. X-ray microanalysis suggests that Pb and Cd are lost from the samples during the preparation process. The diffraction patterns show a small decrease in the lattice parameters, suggesting that a defect structure of the type $Ca_{3\_x}(vac)_xAl_2O_6$ is formed. The distribution of products formed on hydration of the doped $Ca_{3\_x}Mg_xAl_2O_6$ is found to be very different than that observed for the undoped material.

The combustion of waste in cement kilns offers an alternative to disposal or incineration of certain waste streams. This practice is intended to decompose hazardous organic compounds. However, some hazardous waste fuels contain not only toxic organic compounds but also toxic heavy metals. Heavy metals in fuels may be discharged through three separate streams. These include emissions from a kiln through exhaust stacks and their incorporation into cement kiln dust (CKD) and cement clinker. Guo et al., (1996) studied data from a kiln equilibration test that analyzed for heavy metal outputs from a cement kiln co-fired with hazardous waste fuels. Metal outputs from stack emissions, cement kiln dust, and cement clinker were considered. Equations were derived for predicting all three metal outputs at any hazardous waste feed rate under steady state conditions. Through the analysis of two steady state conditions, at the beginning and end of the equilibration test, essentially the same ratios of metal feed rates were found to he distributed to the kiln dust at either high or low metal feed rates. Applying the same distribution ratios in the derived equations, metal concentrations of wasted kiln dust were predicted when the kiln was not using hazardous waste fuels. Measured concentrations of arsenic, beryllium, cadmium, chromium, and lead in wasted kiln dust, at the highest intended hazardous waste feed rates to the kiln, were 68, 10, 72, 18, and 68 times those predicted for feed rates with no hazardous waste. In addition, the intermediate, non-steady state segment of the equilibration test was analyzed. If metals were assumed to not accumulate in the kiln, the intermediate metal concentrations in cement clinker can be predicted to be substantially higher than those at the final steady state.

Nowadays, different kinds of industrial wastes are increasingly used in the clinkering process by the cement industry, with the aim of taking advantage of their energy content or confining unsuitable substances. Trezzaa and Scian (2005) studied the hysicochemical characteristics of the clinkers obtained after incorporating three different wastes in different proportions: two of them with energetic capacity—trade marked waste fuel and waste carbon of petroleum—and the third that would be confined, pyrolitic carbon. The fusion temperature of the mixtures, the differential thermal analysis and the thermogravimetric analysis (DTA/TG) during clinkering and after hydration, the specific surface area at the same milling times, X-ray diffraction (XRD) and mechanical strength of the pastes elaborated with a water/cement 0.4 relation were analyzed. The results obtained were compared to those of the clinker obtained without additions. It was found that pyrolitic carbon is suitable to be loaded with dust into a cement kiln, as it does not alter the final mechanical strength. A slight increase of this value compared to the original one was observed at early on (3 days). Petroleum waste carbon would be suitable to take advantage of its energy; however, it has a slight tendency to damage the final mechanical properties. Fuel mixture generates a greater crystallinity of the principal clinker phases and causes the greater energy requirement of the milling. The better crystallized C3S presence determines the better values of compression strength at early ages. The addition of this kind of wastes requires an excellent control of the temperature in the clinkering zone, because a slight excess of it over that temperature would excessively fluidize the clinker and might cause damages to the refractory lining of the furnace. General, the addition of these wastes, within the percentages and under the conditions of this test, does not significantly alter the clinker properties.

Taweekitwanit (2004) studied and focused on the leaching behavior of heavy metals from cement. The studied heavy metals were chromium, zinc, and nickel. To study the leaching behavior, microwave-assisted leach method 3051A, the availability leaching test (NEN 7341), and the pH static leach test were used. Results showed that chromium and zinc were likely to be leached from the cement, and more than 80% of their content can be leached to the environment. In contrast, approximately 3% of nickel can be leached to environment. From the pH static leach test, chromium was effectively leached at pH 4 to 10. Zinc and nickel were effectively leached at pH 4 and their leachability decreased when the pH increased. In this research, the toxicity characteristic leaching procedure (TCLP) and the leaching test described in the Notification of Ministry of Industry No.6 B.E. 2540 were also used to identify the cement as hazardous waste or non-hazardous waste. The results showed that when the raw materials were doped with more than 0.1 wt.% of chromium, the cement was classified as hazardous waste. In contrast, when the raw materials were doped with up to 2 wt.% of nickel and zinc the cement was not classified as hazardous waste.

Asavapisit and Chotklang (2004) investigated the potential utilization of alkali-activated pulverized fuel ash as a solidification binder to treat electroplating sludge. Compressive strength and leachability of heavy metals from the solidified electroplating sludge were determined to assess the potential for utilization. Metals leaching from the solidified wastes were assessed using the toxicity characteristic leaching procedure (TCLP). The results showed that lead, cadmium and copper were not found in the toxicity characteristic leaching procedure leachates. Chromium, zinc and ferric were detected. In some cases, chromium exceeded U.S. EPA allowable limits.

Combustion chamber dynamics during rotary kiln incineration was studied by Cundy et al. (1989). This study discusses in some detail the research effort performed to date in two of the sub-programs: full-scale in situ sampling and kiln-simulator experimentation. Full-scale in situ measurements are obtained from the Louisiana Division rotary kiln facility of Dow Chemical USA, located in Plaquemine, Louisiana. Summary results obtained from controlled experiments that were performed during continuous processing of carbon tetrachloride and preliminary results obtained during batch mode processing of toluene-laden sorbent packs are presented. Kiln-simulator data are obtained by using the facilities of the Chemical Engineering Department at the University of Utah. The 73 kW natural gas fired rotary kiln simulator is constructed in three refractory lined steel sections with the core of the main section sized at 0.61 m in diameter and 0.61 m long. A schematic of the kiln is shown in Figure 2.9. The burner and main sections rotate from 0.5 to 2.0 rpm, and the exhaust section remains stationary. A rear loading chute (a half pipe of 20 cm diameter) allows a charge of waste to be placed in the center of the main section of the kiln-simulator. Recent kiln-simulator work, conducted in support of the full-scale measurements sub-program, has aided in providing an understanding of the results that have been obtained at the full-scale. Modeling efforts, conducted at Louisiana State University and the University of Utah, have concentrated on the development of realistic, fluid-flow and heat-transfer models, near-term chlorinated kinetic models, and bed mass-transfer models to be incorporated into a global three-dimensional kiln-simulator model. The paper concludes with an overview of these modeling efforts as show in Figure 2.10.

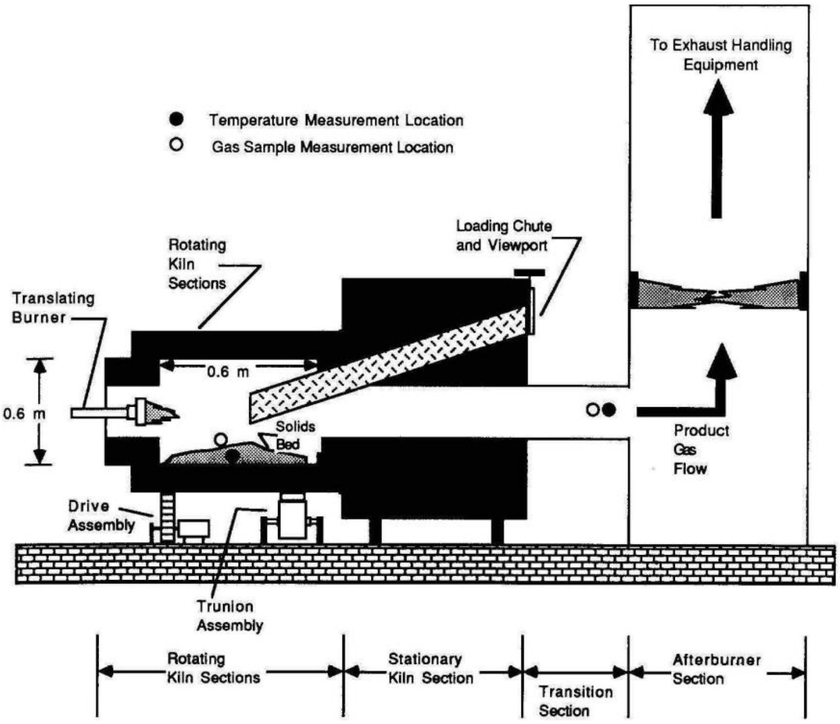


Figure 2.9: The University of Utah’s rotary kiln-simulator

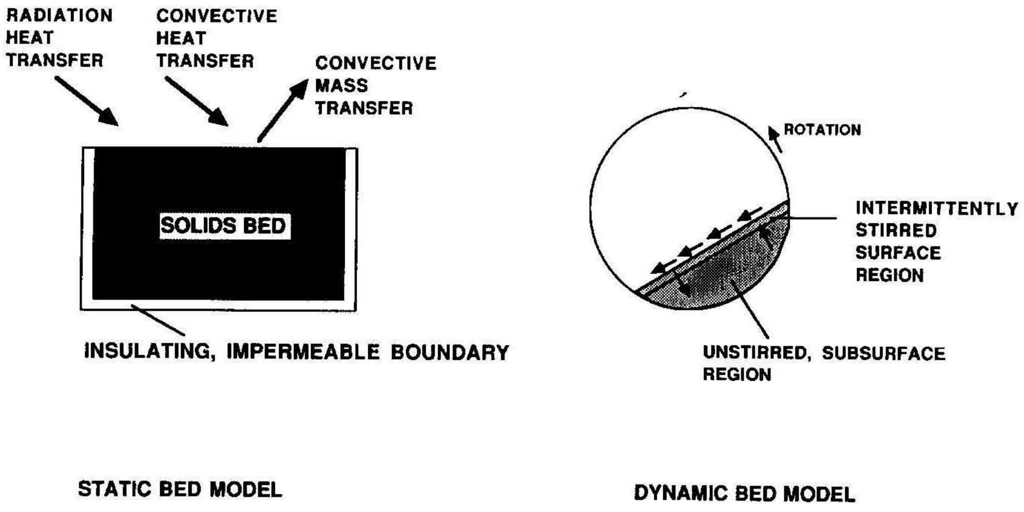


Figure 2.10: The fluid-flow and heat-transfer models

Post-consumer carpet is a potential substitute fuel for high temperature thermal processes such as cement kilns and boilers. In addition, the cleanup of contaminated buildings can result in the need to dispose of potentially significant quantities of carpet, which may or may not be contaminated, and will possibly have decontamination chemicals present. Data gaps exist regarding the potential for the production of increased levels of oxides of nitrogen (NOx), organic pollutants such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs), and engineering issues such as pre-sizing requirements for the carpeting in order to achieve effective combustion. To respond to these data gaps, the US EPA, in collaboration with the Carpet and Rug Institute (CRI) and the Georgia Institute of Technology, performed experiments to address some of these data gaps. Paul M. Lemieux reported on results examining the emissions of PCDDs/Fs from a series of pilot-scale experiments performed at the EPA's rotary kiln incinerator simulator (RKIS) facility at Research Triangle Park, North Carolina. The RKIS has been used in the past to test a wide variety of solid and liquid wastes. The RKIS (as shown in Figure 2.11) consists of a 73 kW (250,000 Btu/hr) natural gas-fired rotary kiln section and a 73 kW (250,000 Btu/hr) natural gas-fired secondary combustion chamber (SCC). Following the SCC is a long duct that leads into a dedicated flue gas cleaning system (FGCS) consisting of another afterburner, baghouse, and wet scrubber. The

RKIS is equipped with continuous emission monitors (CEMs) for oxygen (O2), carbon dioxide (CO2), carbon monoxide (CO), nitrogen oxides (NOx), and total hydrocarbons (THCs). A series of Type-K thermocouples monitor the temperature throughout the system. For the initial tests, the rotary kiln combustion air was flowing at a rate of 85.0 sm3/hr (3000 scfh) and the main burner natural gas fuel was flowing at a rate of 5.66 sm3/hr (200 scfh). The static pressure in the rotary kiln section was maintained at -0.05 in. w.c. For the purposes of these tests, the SCC was not operated, and the temperature in the transfer duct was maintained at approximately 300-350°C (572-662 °F) to promote the formation of PCDDs/Fs so that the differences between the test conditions could hopefully be maximized (Lemieux, 2004).

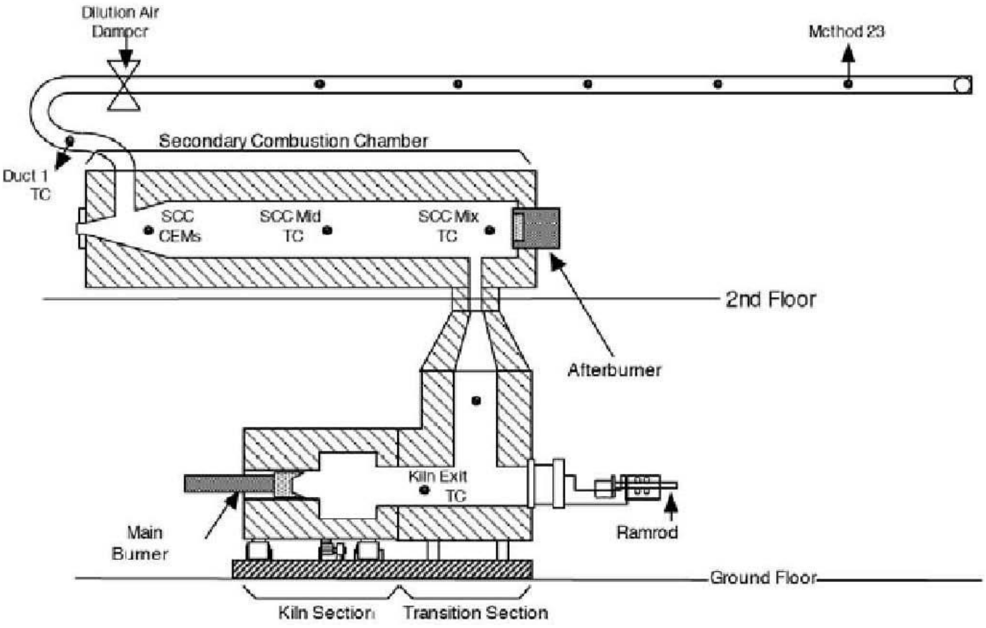


Figure 2.11: Rotary kiln incinerator simulator

Sprung (1985) studied the behavior of arsenic, cadmium, chromium, lead, nickel, thallium, and zinc. Most of these metals fed into the raw material were retained in the clinker and cement kiln dust. The result indicated that the distribution of a metal between the clinker and the cement kiln dust depend on the quantity of the metal fed into the kiln, the chloride content, or the manufacturing process. For example, the distribution of zinc, arsenic, chromium and nickel was relatively insensitive to both the production process and the chloride content, and was largely bound in the clinker.

Von Seebach and Tompkins (1991) investigated the fate of metals in the cement kiln system. Three dry process cement kilns equipped with precalciners, two dry process cement kilns equipped with preheaters, and one wet process cement kiln was used in the investigation. The metals investigated were antimony, arsenic, barium, beryllium, cadmium, chromium, lead, nickel, selenium, silver, vanadium, and zinc. The total input and output of the metals were analyzed to estimate the retention in the process solids versus the concentrations in the emission. The results show that greater than 99% of the metals were retained in the process solids. No difference in the emissions of these metals was noted when portion of the coal was replaced by hazardous waste fuel.

Murat et al. (1996) examined the effects of large additions of Cd, Pb, Cr and Zn to Portland cement raw meal on the composition and properties of clinker. The results showed that a large amount of chromium (84%) was trapped and 53% of zinc was fixed in Portland cement clinker. Also, ZnO addition increased the alite size crystals.

Rachakornkij (2000) found that concentration of leached lead from raw Municipal solid waste incinerator fly ash failed to meet the TCLP limits. However, after stabilized in cement mortars, concentrations of all regulated metals passed the test.

Wang et al. (2000) investigated the leachability of chromium (VI) from solidification chromium (VI) with cement. The toxicity characteristic leaching procedure (TCLP) was used to observe the leachability of chromium (VI). The results concluded that the leachability of chromium (VI) during TCLP testing was dependent on the initial concentration and the time. They also concluded that the K_2CrO_4/cement ratio should not be higher than 0.2% in order not to exceed the chromium concentration of 5 ppm established by the TCLP limit.

CHAPTER III

METHODOLOGY

3.1 Raw materials

Experimental raw meal of OPC Type I (kiln feed) was calcined in cement kiln of manufacturing for preheating at 900°C and taken from the Siam City Cement Public Company Limited (SCCC) Plant, located on 99 Moo 9, Friendship Highway, Tabkwang, Kaengkoi, Saraburi. Four series of heavy metals and combinations of heavy metals (metal oxide) are shown in Table 3.1, Cr (Cr_2O_3), Cu (CuO), Ni (NiO_2), and Zn (ZnO), and combinations of heavy metals no. 5 & 6. They were mixed with raw meal (called "mixture") and a control one (without metal addition, called "control"). The mixtures were homogenized and the concentration of each heavy metal varied as shown in Table 3.2.

Table 3.1: Chemicals used in this research

Item	Chemical name	Formula	Purity
1	Chromium (III) Oxide	Cr_2O_3	98%
2	Copper (II) Oxide	CuO	98%
3	Nickel (II) Oxide	NiO_2	96%
4	Zinc Oxide	ZnO	99%
Combinations of Heavy Metals			
5	Combination of Ni:Cr:Cu:Zn ratio 1:1:1:1	NiO_2:Cr_2O_3:CuO:ZnO	
6	Combination of Ni:Cr:Cu:Zn ratio 1:3:5:7	NiO_2:Cr_2O_3:CuO:ZnO	

Table 3.2: Varying concentrations of hazardous materials in kiln feed.

Item	Hazardous Material name	Literature	Cement Plant	Experimental 4-5 concentration per each Heavy Metal (ppm)					
		ppm	ppm	Control	1	2	3	4	5
1	Cr2O3	50,000	SCCC 500 Other 5,000	Control	1,000	5,000	10,000	20,000	_
2	NiO2	TCLP 20x1,000	SCCC 1,000 Other 10,000	Control	1,000	5,000	10,000	20,000	_
3	CuO	TCLP 25x1,000	SCCC 500 Other 20,000	Control	1,000	5,000	10,000	20,000	_
4	ZnO	TCLP 250x1,000	SCCC 3,000	Control	1,000	5,000	10,000	20,000	_
5	NiO_2 : Cr_2O_3 : CuO : ZnO	ratio 1:1:1:1		Control	500	3,000	5,000	10,000	20,000
6	NiO_2 : Cr_2O_3 : CuO : ZnO	ratio 1:3:5:7		Control	500	3,000	5,000	10,000	20,000

3.2 Instrumentations

3.2.1 Pilot-scale rotary cement kiln

A pilot-scale rotary cement kiln was designed for this study. It was constructed by the Siam City Cement Public Company Limited (SCCC). The pilot-scale rotary cement kiln and the building were installed at 99 Moo 9, Friendship Highway, Tabkwang, Kaengkoi, Saraburi, as shown in Figure 3.1 and 3.2. The building has an area of about 72 m^2 (6 meters (width) x 12 meters (length) x 6 meters (height)). For the pilot-scale rotary cement kiln, it consisted of a rotary kiln, clinker cooler, burners, lifter and cooling tower. Its hot air outlet chamber has an inside circle diameter of about 0.60 meters x 0.60 meters (length). The rotary kiln has an inside circle diameter of about 0.60 meters x 1.0 meter (length) as shown in appendix A, rotating at 0.5 rpm (revolutions per minute) and the fuel used was LPG (Liquified Petroleum Gas). The clinker cooler rectangular chamber has inside diameter of about 1.6 meters (length) x 1 meter (width) x 1.3 meters (height). Natural air was used to decrease temperature of clinker. The cement kiln dust (CKD) was trapped by water in cooling tower.

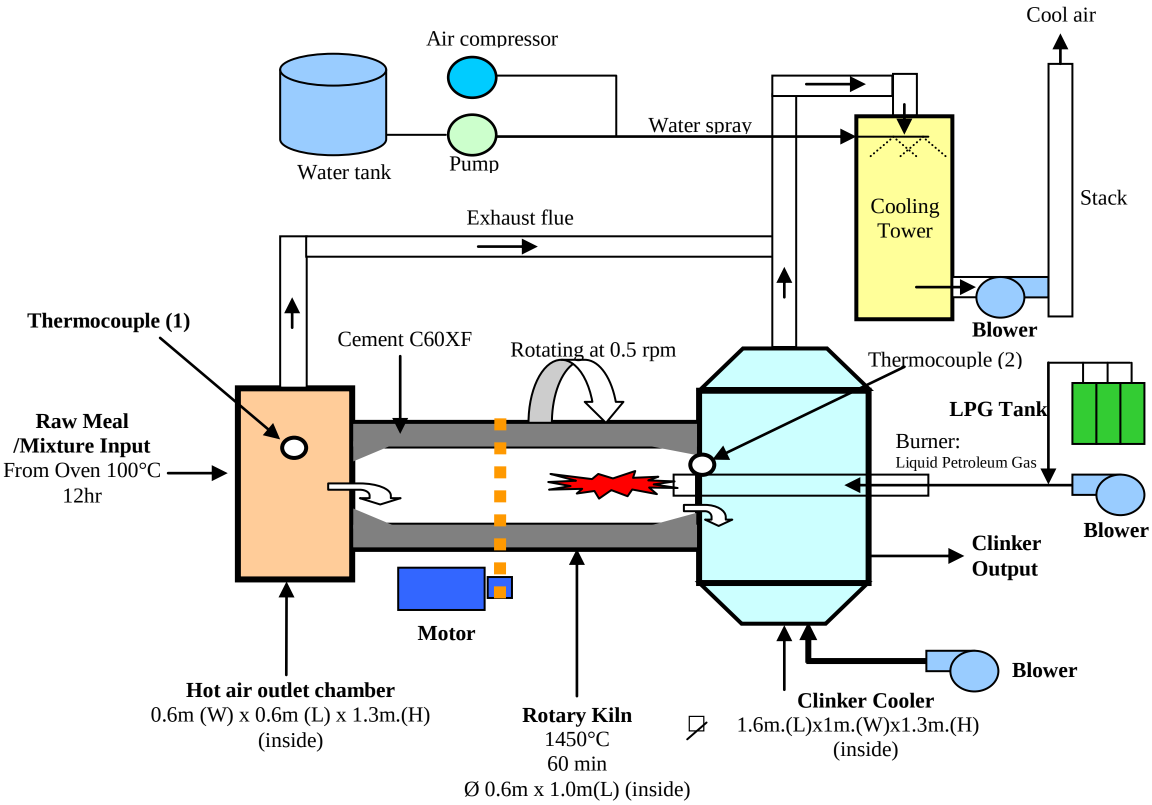


Figure 3.1: Flow diagram of the pilot-scale rotary cement kiln

Figure 3.2: The pilot-scale rotary cement kiln

3.2.2 V-mix machine

The mixture (1 kg of sample) of kiln feed and metal oxides was mixed with V-Mix machine, Patterson-Kelley model type Blend Master B-Lab blender, to make mixture homogeneous as shown in Figure 3.3.

Figure 3.3: The V-Mix machine

3.2.2 The swinging mill machine and tablet pressing machine

The swinging mill machine was used for grinding clinker. By grinding 20 grams per batch after that the powder samples were analyzed for total concentrations (TC) and their leachates by Waste Extraction Test (WET) according to the Thai regulations (B.E. 2548). Then, the results were compared against Total Threshold Limit Concentration (TTLC) and Soluble Threshold Limit Concentration (STLC) that list standard concentrations for each metals. Also to be compressed with the tablet pressing machine (Figure 3.5) before importing to analyze by XRF and XRD.

Figure 3.4: The swinging mill machine

Figure 3.5: Tablet pressing machine

3.2.3 Lab ball mill machine

The lab mill machine (Figure 3.6) was used for grinding the clinker samples. By grinding 2 kilograms per batch after that the powder samples were analyzed for blaine fineness which was controlled to be more than 3300 cm^2/g or in the range of 3400±100 cm^2/g. Then, samples passing the criteria were mixed and formed mortars for subsequent compressive strength tests.

Figure 3.6: Lab ball mill machine

3.3 Method of data collection and analysis

The mixtures were left in an oven at 100°C for 12 hours and burned in a pilot scale rotary cement kiln of preheating at 700°C - 900°C for 10 minutes from the time this temperature was reached. Finally, they were burned at 1450°C for 60 minutes and quenched in a clinker cooler; the final products of this experimental were clinkers. The clinkers were kept in a moisture-free container until testing as shown in Table 3.2. The application concentrations of each heavy metal in the mixture that can be co-processed by a cement kiln without affecting the quality of the clinker were considered. The maximum metal concentrations allowed in the Thai regulatory leaching procedure are health-based standards as shown in Table 3.4 and Table 3.5. Finally, the clinker was analyzed using the ICP, XRF, XRD, SEM, and the physical properties of cement were analyzed such as blaine fineness, compressive strength, etc. as shown in Table 3.3. Figure 3.7 described the steps for producing clinker. Finally, simple equations were prepared in terms of concentration of heavy metals in solid waste that has been mixed with raw meal before burning and the clinker after burning. Both can be applied to a real hazardous waste management situation which involves a full-scale rotary cement kiln and creates the standard of concentration value of heavy metals in solid wastes and raw meal, which can be burned in a rotary cement kiln.

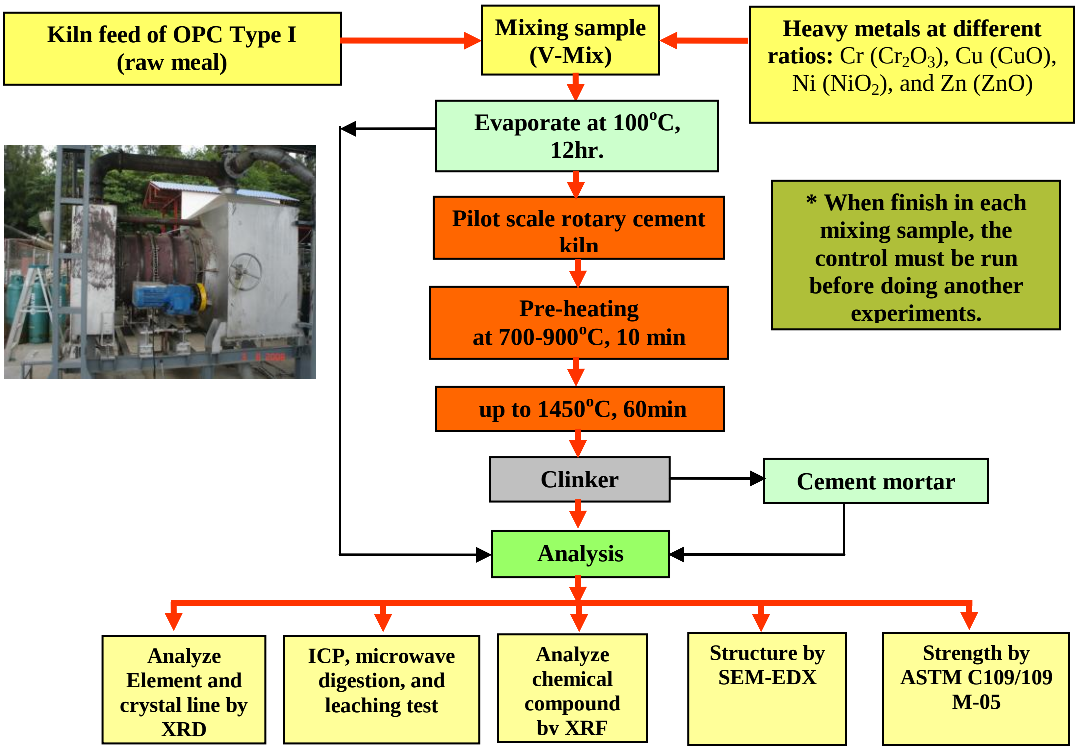


Figure 3.7: The steps for producing clinker

Table 3.3: The method of analysis.

Analysis	Control (Blank)	Before burning (Mixtures)	After burning (Clinker)	After test strength (Concrete)
1. Heavy Metal (Cr, Cu, Ni, and Zn) by the inductive couple plasma (ICP) (total on waste) and Thai regulatory leaching procedure in the Notification of Ministry of Industry B.E. 2548 on Management of Wastes	test	test	test	test
2. % Moisture	test	test	test	-
3. Scanning electronic microscopy (SEM)	test	test	test	-
4. X-ray fluorescence spectrometry (XRF)	test	test	test	-
5. X-ray diffraction (XRD)	test	test	test	-
6. ASTM C109/C109M-05	test	-	test	-

Table 3.4: Acceptable metal concentrations in cement (Environmental Science, 1991).

Constituent	Acceptable Level (mg/kg)
Antimony	50,000
Arsenic	200
Barium	50,000
Beryllium	50
Cadmium	1,000
Chromium III	50,000
Chromium VI	100
Lead	5,000
Mercury	5,000
Silver	1,000
Thallium	10,000

Table 3.5: Metal concentration limits in the Thai regulatory leaching procedure and the TCLP (U.S. EPA, 1991).

Metal	Concentration (ppm) (U.S. EPA, 1991)	Concentration (ppm) (Thai standards)
Antimony	1	-
Arsenic	5	5[a]
Barium	100	100[a]
Beryllium	0.007	0.75[a]
Cadmium	1	1[a]
Chromium	**5**	**5[a]**
Lead	5	5[a]
Mercury	0.2	0.2[a]
Nickel	**70**	**20[a]**
Selenium	1	1[a]
Silver	5	5[a]
Thallium	7	7[a]
Copper	**-**	**25[a]**
Vanadium	-	24[a]
Zinc	**-**	**250[a]**

Remark: [a] Metals are used in Thai standard which are classified hazardous waste by Waste Extraction Test (WET). Notification of Ministry of Industry B.E. 2548 on Management of Wastes.

3.3.1 TTLC - Total Threshold Limit Concentration

TTLC-this analysis determines the total concentration of each target analyzed in a sample. Samples are analyzed using published EPA methods 3052 by which this method utilized a microwave digester for digesting the compounds that contain silica and organic compounds. The materials used in this procedure comprised vessel Teflon, 100-1000ml of volumetric flasks, funnels (polypropylene), 65% of HNO_3, HF, HCl, and 0.87 M of H_3BO_3. First, the 0.87 M of H_3BO_3 was prepared by 53.465 g of 96% of H_3BO_3 in powder form was weighed. De-ionized water was then poured into the 1000 ml of volumetric flask that contained the H_3BO_3 sample. 0.5 g clinker samples were weighed. Next, the samples were digested using microwave digestion. Digestion involved a 2 steps process as shown in Figure 3.8. This method used for extracting of heavy metals inside the samples, after that the liquid of extraction was sent to analyze by using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) VARIAN model type VISTA-MPX Axial EL02086289 as shown in Figure 3.10 to determine the concentrations of Cr, Ni, Cu and Zn in all samples inside the clinker product and was used to measure initial concentration of each heavy metal in the kiln feed as well. When any target analyzed exceeds the TTLC limits, the waste is classified as hazardous and its waste code is determined by the compound(s) that failed TTLC. The results of this analysis can be used to determine for STLC level which is necessary by comparing 10 times the STLC limit to the TTLC results. A factor of ten is necessary to compensate for a 1:10 dilution factor that is present in one analysis but not the other. If the TTLC results do not exceed 10 times the STLC limit then normally no further analysis is required.

3.3.2 STLC - Soluble Threshold Limit Concentration

This analysis determines the amount of each analyst that is soluble in the "Waste Extraction Test", (WET) leachate. This WET leachate procedure is used for solid samples or for samples containing > 0.5% solids. The sample is tumbled in 10 times its weight of a 0.2M sodium citrate buffer for 48 hours. This leachate is then analyzed to determine the soluble concentrations. The steps of Waste Extraction Test B.E. 2548 (Anonymous, 2006) are shown in Figure 3.9, after that the liquid of extraction was sent to analyze by using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) VARIAN model type VISTA-MPX as shown in Figure 3.10 to determine the concentrations of Cr, Ni, Cu and Zn in all samples.

3.3.3 Analyses of the structure and chemical properties of samples by XRD, XRF, and SEM

X-ray fluorescence (XRF) spectrometer and X-ray diffraction (XRD), Thermo model type ARL 9900 OASIS total cement analyzer as shown in Figure 3.11, are basic instruments for analyzing the chemical properties of cement. Around 50 g of the clinker sample was ground by the swinging mill to reduce the size of clinker in 30 seconds. Then, around 20 g of clinker sample was milled by the swinging mill again at 30 seconds for analyzing the free lime content. Bromine was added to another 20 g of clinker sample to trap the clinker, and it was milled for 3 minutes to analyze the total concentration of chemicals inside the clinker. XRF was used for analyzing the chemical oxides, whereas XRD was used for analyzing the free lime and chemical compositions.

Part of the clinker was used in polished sections for scanning electron microscopy (SEM) via JEOL model type JSM-5800LV as shown in Figure 3.12 was used for analyzed particle morphology, phase of cement and quantity of heavy metals in clinker by cutting the surface of the clinker.

3.3.4 Analysis of compressive strength of the Portland cement by ASTM C109/C109M-05

This standard method for determining compressive strength of hydraulic cement mortar uses 2-in or 50 mm. cube specimens. The temperature for testing was maintained at 23 ± 3.0^{o}C (room temperature). The humidity should not be less than 50%. The clinker samples were ground by a ball mill and mixed with 5% by weight of gypsum to control the setting time of the cement. This test was repeated three times. The quantities of materials that were mixed at one time in a mortar for making the nine test specimens as shown in Table 3.6 consists of cement 740g, sand 2035g and water 359 ml.

The cubic shape of the cement samples were tested on day 1, day 3, day 7, and day 28 by using compression machine (Figure 3.13). All test specimens for a given test age was broken within the permissible tolerance prescribed as follows (ASTM C109/C109M-05, 2005):

Test Age	Permissible Tolerance
24 hours	±1⁄2 hour
7 days	±3 hours
28 days	±12 hours

The compressive strength of the samples was tested using the strength machine and the results were compared with the standard of the manufacturing and the Thai Industrial Standard Institute (TIS-15, 1989) as shown in Table 3.7.

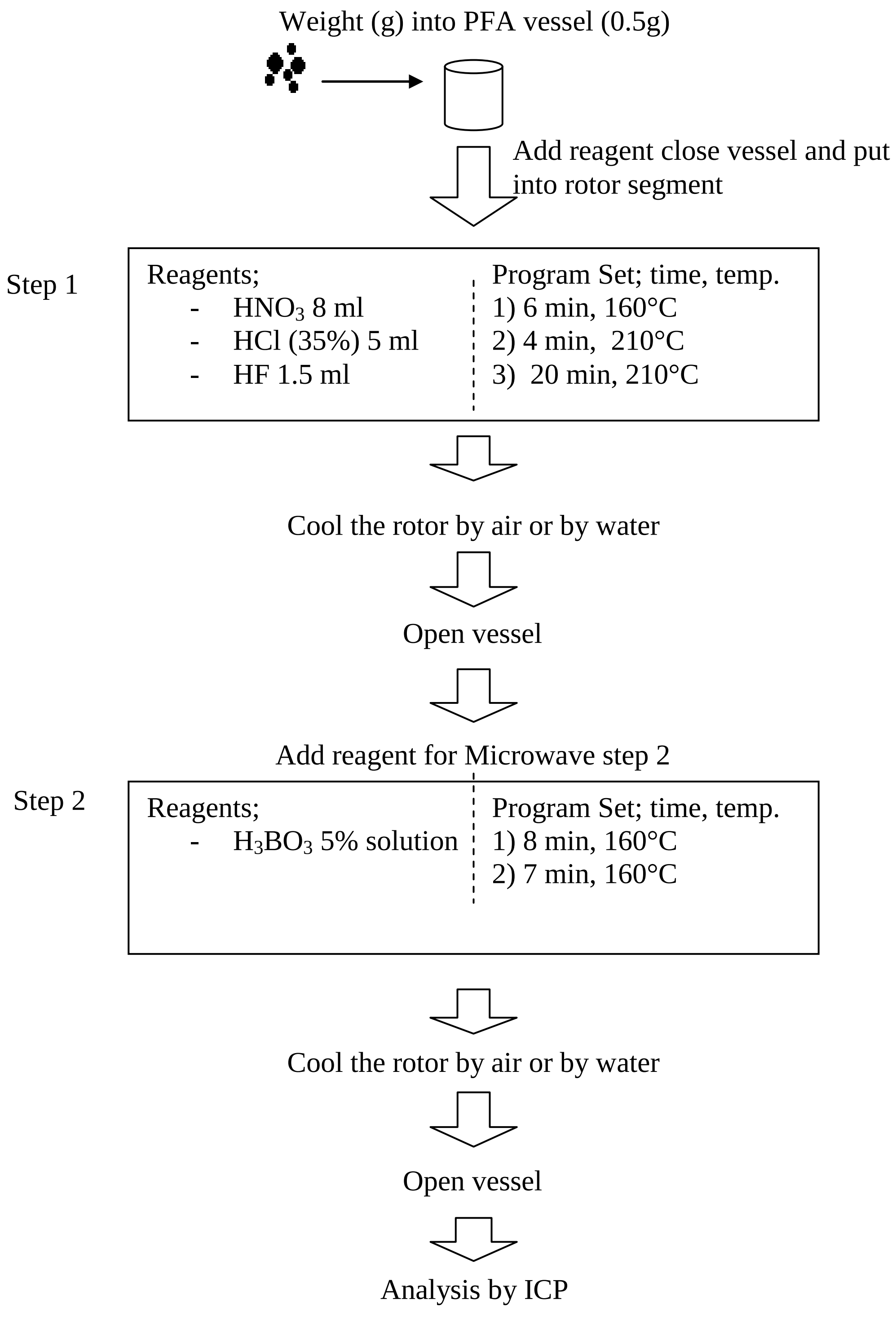
Table 3.6: Composition of a mortar for testing the compressive strength.

Cement	740 g
Sand	2035 g
Water	359 ml
Water-cement ratio	0.485

Table 3.7: The compressive strength values at specific times.

Time (day)	Manufacturing standard of compressive strength (kg/cm^2)	Thai standard of compressive strength (kg/cm^2)
1	>130	>85
3	>220	>120
7	>280	>150
28	>400	> 245

Flow chart for EPA 3052



Weight (g) into PFA vessel (0.5g)

Add reagent close vessel and put into rotor segment

Step 1

Reagents;
- HNO_3 8 ml
- HCl (35%) 5 ml
- HF 1.5 ml

Program Set; time, temp.
1) 6 min, 160°C
2) 4 min, 210°C
3) 20 min, 210°C

Cool the rotor by air or by water

Open vessel

Add reagent for Microwave step 2

Step 2

Reagents;
- H_3BO_3 5% solution

Program Set; time, temp.
1) 8 min, 160°C
2) 7 min, 160°C

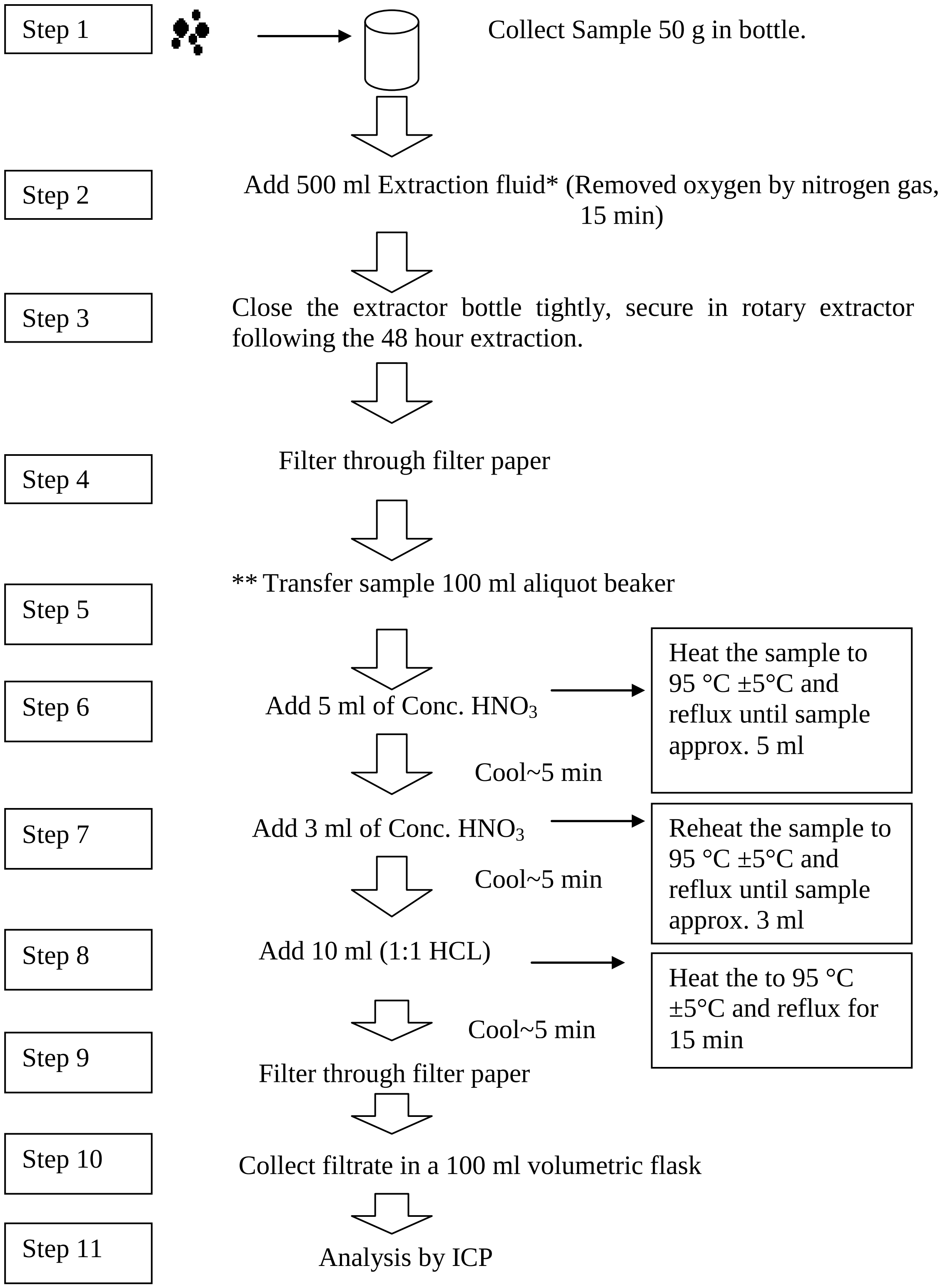
Cool the rotor by air or by water

Open vessel

Analysis by ICP

Figure 3.8: The steps of the EPA 3052 method for analyzing total heavy metal

Flow chart of Waste Extraction Test



Step 1 Collect Sample 50 g in bottle.

Step 2 Add 500 ml Extraction fluid* (Removed oxygen by nitrogen gas, 15 min)

Step 3 Close the extractor bottle tightly, secure in rotary extractor following the 48 hour extraction.

Step 4 Filter through filter paper

Step 5 ** Transfer sample 100 ml aliquot beaker

Step 6 Add 5 ml of Conc. HNO_3 → Heat the sample to 95 °C ±5°C and reflux until sample approx. 5 ml

Cool~5 min

Step 7 Add 3 ml of Conc. HNO_3 → Reheat the sample to 95 °C ±5°C and reflux until sample approx. 3 ml

Cool~5 min

Step 8 Add 10 ml (1:1 HCL) → Heat the to 95 °C ±5°C and reflux for 15 min

Cool~5 min

Step 9 Filter through filter paper

Step 10 Collect filtrate in a 100 ml volumetric flask

Step 11 Analysis by ICP

Remark : * Extraction fluid preparation : 0.2 M sodium citrate pH 5 ± 0.1(Citric acid mix 4.0 N NaOH PH of fluid willbe 5.0)
** Reference method EPA publication SW-846(Method 3010A:Acid digestion of aqueous sample and extract for total metals for analysis by FLLA or ICP spectroscopy)

Figure 3.9: The steps of Waste Extraction Test B.E. 2548 (Anonymous, 2006)

Figure 3.10: Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Figure 3.11: The combination machine of XRF and XRD

Figure 3.12: Scanning Electron Microscope (SEM)

Figure 3.13: Compression machine

3.3.5 Equations using in this study

a. Concentration of metal oxide, LSF, SM and AM in kiln feed:

Concentration of metal oxide (ppm) = [(mass of metal oxide) x (atomic weight / molecular weight) / 1000g of kiln feed] x 10^6

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

Silica modulus (SM) = % SiO_2 / (%Al_2O_3 + %Fe_2O_3)

Alumina modulus (AM) = % Al_2O_3 / %Fe_2O_3

b. Compressive strength:

ASTM: Strength: kg / cm^2 = KN x 1000 / (25 x 9.81)

MPa = N / mm^2 = Psi / 145 = 0.1 Kg / cm^2

If area of mortar is between 24.62 – 25.37 cm^2 (over 1.5%),

Strength: kg / cm^2 = KN x 1000 / (Area x 9.81)

CHAPTER IV

RESULTS AND DISCUSSION

In order to investigate the effect of heavy metals in clinker and use the obtained information to illustrate the total concentration and the leaching behavior of heavy metals from the control clinker, the experimental clinkers were made with similar characteristic comparing with the clinker from cement manufacturing. So, the optimum condition for experimental clinker in the pilot-scale rotary cement kiln was found. The varied parameters for experimental clinker were burned in the same condition of temperature and burning period. Analysis of total concentration, extraction concentration, free lime content, XRF, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and compressive strength were used to compare the characteristics of the obtained clinker. The study results of the samples are presented in the following subsections.

4.1 Raw material preparation

Kiln feed of OPC Type I (raw meal) which was passed pre-calcinations process, was collected from the Siam City Cement Public Company Limited (SCCC). The X-ray fluorescence spectrometer (XRF) was used to analyze the chemical composition in the kiln feed was showed in Table 4.1. Lime saturation factor (LSF), silica modulus (SM), and alumina modulus (AM) that serve as indication of combinability and burn-ability of feed mixtures in burning at the pilot scale rotary cement kiln. The result showed that LSF, SM and AM of kiln feed were 90.00, 2.45 and 1.31 respectively. However, the main chemical compositions of kiln feed which are important such as SiO_2, Al_2O_3, Fe_2O_3 and CaO were equal to 15.61%, 3.61%, 2.76% and 44.85%, respectively. As the result LSF of kiln feed was in the range of standard cement which LSF was in the range of 90 to 100 and the typical ranges of chemical compositions for raw meal were 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 (Hewlett, 2004; Amiri, 2008). Thus, the kiln feed was suitable for burning in the pilot-scale rotary cement kiln. The concentration of heavy metals in raw meal was shown in Table 4.2 such as 45.53 ppm of Cr, 72.86 ppm of Cu, 157.43 ppm of Zn and 25.73 ppm of Ni. The amount of metal oxide was added to kiln feed (raw meal) in the proportions were set on 1000, 5000, 10000 and 20000 ppm. And the experiments were conducted with four types of heavy metal that the simulated proportion of wastewater sludge from electronic industry and also the different ratios of heavy metals to simulate with the sludge like steel industry. The moisture content is very low only 0.09%. The loss on ignition (LOI) is a good indicator to show percent loss of the weight of kiln feed and samples before burning at 1450°C, so the LOI of kiln feed was 30.56%. The result showed that the weight 1 kg of kiln feed with added heavy metals was decreased about 30.56%, so the weight of clinker was remained 0.69 kg. Because after burning most of the weight loss could be attributed to the evaporation of moisture and the reaction in burning process between $CaCO_3$ to be CaO and CO_2 or exhaust gas. Evaporation of carbon dioxide and the element at a low boiling point caused the loss of weight in the kiln feed and increased percent concentration of chemical oxide and concentration of heavy metals inside the clinker. In addition, the cement kiln dust (CKD) caused the loss of weight of the kiln feed to form clinker as well. Because the CKD could be blown out together with exhaust gas and was trapped by water at air cooling tower.

Table 4.1: The percent chemical compositions of the collected kiln feed which was passed pre-calcinations process.

Chemical composition	Quantity
SiO_2 (%)	15.61
Al_2O_3 (%)	3.61
Fe_2O_3 (%)	2.76
CaO (%)	44.85
MgO (%)	1.12
K_2O (%)	0.43
Na_2O (%)	0.13
SO_3 (%)	0.69
TiO_2 (%)	0.094
P_2O_5 (%)	0.080
Mn_2O_3 (%)	0.048
Cl (%)	0.022
LOI (%)	30.56
SUM	100.00
LSF	90.00
SM	2.45
AM	1.31
S/A	4.32
Na_2Oeq (%)	0.42

4.2 The comparison of concentrations of heavy metals in kiln feed, clinker and cement mortar

At currently, the raw meal contains some heavy metals, EPA 3052 was the method used for analyzing the concentrations of heavy metal inside the clinker product and was used to measured initial concentration of each heavy metal in the raw meal as well. The concentration of heavy metal in the raw meal control was showed in Table 4.2. Moreover, the total heavy metal in raw meal after adding with different ratios of four metal oxides was analyzed to know the real value in mixed raw meals.

Table 4.2: Concentration of heavy metal in the control raw meal and in the control clinker that analyzed by EPA 3052, TC and WET.

Heavy metal	Control kiln Feed		Control clinker			Thai's standard		SCCC's standard
	TC (ppm)	SD	TC (ppm)	SD	WET (ppm)	TC (ppm)	WET (ppm)	Total heavy metal in clinker (ppm)
Cr	45.53	4.37	78.42	14.83	ND	2500	5	270
Cu	72.86	2.29	130.94	15.01	ND	2500	25	280
Zn	157.43	4.62	229.56	19.99	ND	5000	250	370
Ni	25.73	1.66	39.34	9.70	ND	2000	20	101
As	13.01	2.56	37.81	1.67	ND	500	5	40
Se	ND	3.57	ND	2.13	ND	100	1	-
Ba	46.33	1.80	82.09	1.54	1.01	10000	100	-
Pb	15.12	2.38	19.05	1.97	ND	1000	5	50
V	16.92	1.45	43.02	2.10	ND	2400	24	150
Sb	ND	-	ND	-	ND	500	5	-
Tl	ND	-	ND	-	ND	700	7	0.04
Cd	4.26	1.23	6.84	1.36	ND	100	1	1.5
Hg	ND	-	ND	-	ND	20	0.2	0.005

Remark: ND = Not detectable

TC and WET are used when determining the hazardous waste characterization under California State regulations as outlined in Title 26 of the California Code of Regulations (CCR). TCLP is the characterization based on Federal guidelines. These apply to organic as well as inorganic analysts. The intent of the leachate procedures are to simulate the conditions that may be present in a landfill where water may pass through the landfill waste and travel on into the groundwater carrying the soluble materials with it.

The result of different ratios of heavy metals was showed in Table 4.3 to 4.14 and Figure 4.1 to 4.12. Due to the evaporation of easily volatized compounds in the raw meal during the burning process, the concentration of heavy metals in the clinker was higher than the heavy metals inside the kiln feed before the burning process because during the burning process the compounds were reacted and some of them were evaporated such as CO_2 and volatized compounds, so the volume and the weight of clinker have reduced lower than kiln feed are about 30-40%. The heavy metals were found in the clinker and cement mortar at different ratios. However, the concentration of heavy metals in clinker must not be over Thai's standard for classification of hazardous waste as shown in Table 4.2 such as concentration of Ni, Cr, Cu and Zn in clinker must be less than 2000, 2500, 2500 and 5000 ppm, respectively (Anonymous, 2006). Moreover, the results of leachate testing by WET were shown that the concentrations of heavy metals in clinker and cement mortar were not over standard.

4.2.1 The comparison of concentrations of Cr in kiln feed, clinker and cement mortar

Figure 4.1 and Table 4.3 shows the results obtained from total concentration of chromium in the kiln feed, the clinker and cement mortar were only added with chromium oxide. The result shows the amounts of chromium increased and detected from control, 1000, 5000, 10000, and 20000 ppm of initial concentrations of chromium doped in kiln feed were 45.53, 1089, 4995, 10057, and 20248 ppm respectively, whereas total concentration of chromium in clinker was increased to 78.42, 1678, 7448, 15071, and 28499 ppm respectively. However, total concentration of chromium in cement mortar was decreased to ND, 462, 2015, 4093, and 8351 ppm respectively. Because of cement mortar was mixed with sand the concentration of chromium in cement can be diluted. The result showed that the concentration of Cr was in the range of 1000 to 20000 ppm which it was not destroyed in burning process and occurred in clinker. However, the total concentration (TC) of chromium by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. The concentration of Cr in clinker by WET was increased in the range of 0.45 to 2.34 ppm, but it could not be detected in the cement mortar. The result showed that the concentration of Cr was still within the range of Thai's standard (< 5 ppm).

Table 4.3: Analysis of the concentrations of Cr in the kiln feed, the clinker and the cement mortar.

Ratios of Cr (ppm)	Concentration of Cr by TC						Concentration of Cr by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	45.53	4.37	78.42	14.83	19.85	1.90	ND	ND
1000	1089	214.04	1678	139.47	462	33.60	0.45	ND
5000	4995	108.97	7448	129.34	2015	20.00	1.14	ND
10000	10057	170.47	15071	103.29	4093	16.52	2.15	ND
20000	20248	179.02	28499	236.45	8351	32.19	2.34	ND

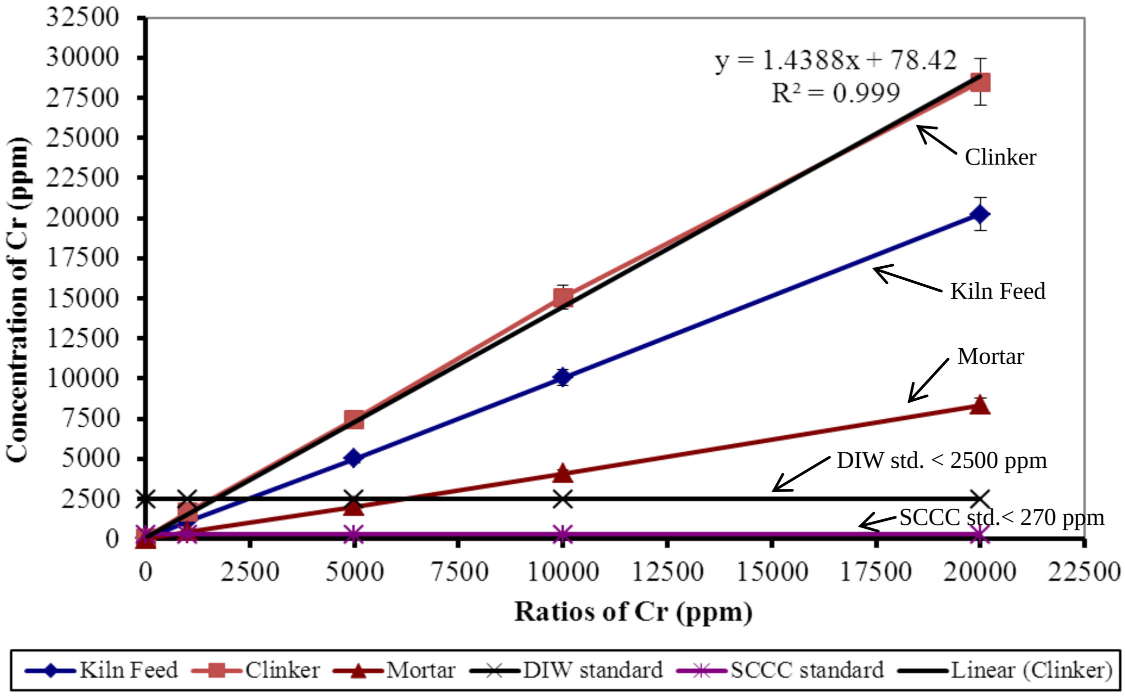


Figure 4.1: Comparison of the concentrations of Cr in the kiln feed, the clinker and the cement mortar

At the first combination ratios of heavy metals (Ni:Cr:Cu:Zn =1:1:1:1) which mixed in kiln feed, the concentrations of Cr were shown in Table 4.4 and Figure 4.2, according to the initial concentrations of chromium doped in kiln feed were in the range of 145 to 5058 ppm, whereas total concentration of chromium in clinker was increased in the range of 274 to 7573 ppm. However, total concentration of chromium in cement mortar was decreased in the range of 95 to 2536 ppm. Thus, chromium occurred in clinker and mortar and the concentration of Cr in the cement mortar less than in clinker because of a combination of sand. Nevertheless, we have to consider the total concentration (TC) of chromium by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of chromium in clinker at 270 ppm. The concentration of Cr in clinker by WET was increased in the range of 0.08 to 1.15 ppm, but it could not be detected in the cement mortar. The result showed that at this combination ratio of heavy metals, Cr was still in the range of Thai's standard (< 5 ppm).

Table 4.4: Analysis of the concentrations of Cr in combination of Ni:Cr:Cu:Zn =1:1:1:1 in the kiln feed, the clinker and the cement mortar.

Ratios of Cr (ppm)	Concentration of Cr by TC						Concentration of Cr by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	45.53	4.37	78.42	14.83	19.85	1.90	ND	ND
125	145	9.85	274	42.32	95.33	7.95	0.08	ND
750	769	40.29	1258	101.42	398	26.23	0.12	ND
1250	1175	25.94	1945	41.68	595	26.29	0.17	ND
2500	2495	63.93	3210	88.83	975	32.05	0.26	ND
5000	5058	100.14	7573	64.97	2536	45.90	1.15	ND

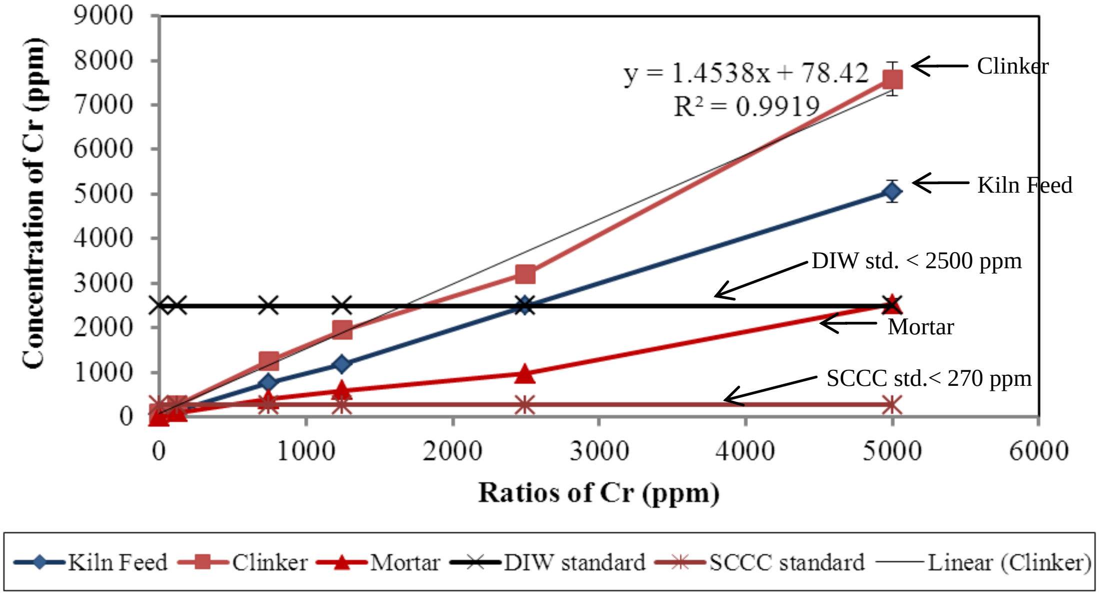


Figure 4.2: Comparison of the concentrations of Cr in combination of Ni:Cr:Cu:Zn =1:1:1:1 in the kiln feed, the clinker and the cement mortar

At the second combination ratios of heavy metals (Ni:Cr:Cu:Zn =1:3:5:7) which mixed in kiln feed, the concentrations of Cr were shown in Table 4.5 and Figure 4.3, the concentrations of chromium doped in kiln feed were in the range of 120 to 3942 ppm, whereas total concentration of chromium in clinker was increased in the range of 255 to 4937 ppm. However, total concentration of chromium in cement mortar was decreased in the range of 85 to 1591 ppm. The results also showed that Cr appeared in the clinker and the cement mortar. Although, the concentration of Cr in clinker by WET was increased in the range of 0.05 to 1.02 ppm, but it could not be detected in the cement mortar which was not over Thai's standard.

Table 4.5: Analysis of the concentrations of Cr in combination of Ni:Cr:Cu:Zn =1:3:5:7 in the kiln feed, the clinker and the cement mortar.

Ratios of Cr (ppm)	Concentration of Cr by TC						Concentration of Cr by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	45.53	4.37	78.42	14.83	19.85	1.90	ND	ND
93.75	120	32.19	255	63.50	85.06	20.82	0.05	ND
562.50	585	99.96	1018	58.08	298	38.20	0.11	ND
937.50	1012	70.49	1776	63.17	553	64.51	0.18	ND
1875.00	1985	118.58	2921	124.06	844	30.51	0.25	ND
3750.00	3942	73.74	4937	73.43	1591	60.70	1.02	ND

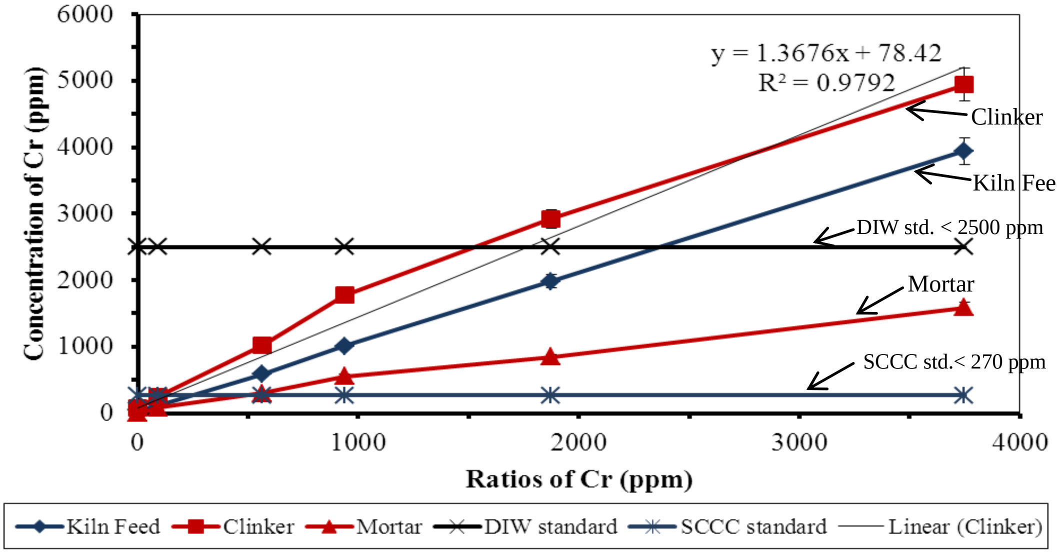


Figure 4.3: Comparison of the concentrations of Cr in combination of Ni:Cr:Cu:Zn =1:3:5:7 in the kiln feed, the clinker and the cement mortar

The results showed that chromium was not destroyed in burning process and occurred in the clinker and the cement mortar. Because of chromium is moderate volatile element (Kolovos et al., 2002) and has high melting and boiling point at 1857°C and 2672°C, respectively. A large amount of chromium (84%) was trapped in Portland cement clinker (Murat and Sorrentino, 1996). Chromium oxides, when added to the clinker raw meal, do not evaporate during the burning process, by which 1% Cr_2O_3, would not affect the emission ratio of these metals, even if the wastes have chlorides, and this oxide would be totally incorporated into the clinker (Barros et al., 2002). The TC of chromium by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. Thus, the total concentration of Cr in kiln feed must be added less than 1665 mg/kg when we use the equation 4.2 as shown below to predict the concentration of Cr in the clinker. Although, the standard of SCCC is normally to control total concentration of chromium in clinker at 270 ppm to control the qualities of cement products.

As the results, the linear equations in term of concentration of chromium (ppm or mg/kg) were prepared as shown below:

$$Y_{Cr} = 1.4388X_{Cr} + 78.42, \quad R^2 = 0.9990 \tag{4.1}$$

$$Y_{Cr} = 1.4538X_{Cr} + 78.42, \quad R^2 = 0.9919 \tag{4.2}$$

$$Y_{Cr} = 1.3676X_{Cr} + 78.42, \quad R^2 = 0.9792 \tag{4.3}$$

Whereas: Y_{Cr} = total concentration of Cr in clinker, ppm
X_{Cr} = total concentration of Cr added in kiln feed, ppm
78.42 = constant of initial concentration of Cr in clinker, ppm
R^2 shows linear equation which approaches 1.

Comparison of three equations as shown above was found to be similar to the linear equation because R^2 approached one. The slope of equation 4.2 was more than the others. The first equation (eq. 4.1) has a concentration of Cr in kiln feed greater than the others was in the range of 45.53 to 20248 ppm and the second equation (eq. 4.2) has concentration of Cr in kiln feed was in the range of 45.53 to 5058 ppm and the third equation (eq. 4.3) has concentration of Cr in kiln feed which was in the range of 45.53 to 3942 ppm.

Thus, the equations 4.1 to 4.3 were used to predict the concentration of chromium in clinker to determine the concentration of chromium was added to the kiln feed and other heavy metals. The proportion that is similar or different which must be checked the suitable for predicting the initial concentration of chromium. If the raw material is only mixed with the chromium which can be predicted from the range of 45 to 20000 ppm by using eq. 4.1. The second equation (eq. 4.2) is suitable for predicting the concentration of chromium if the raw material is mixed with other heavy metals in proportions which is similar to Ni:Cr:Cu:Zn = 1:1:1:1, which is predicted to range from 45 to 5000 ppm, and the third equation (eq. 4.3) is suitable for predicting the concentration of chromium. If the raw material is mixed with other heavy metals in the ratios which is similar to Ni:Cr:Cu:Zn = 1:3:5:7, which is predicted to range from 45 to 4000 ppm. For example, when chromium sludge contained chromium higher than the other heavy metals which is shown from the analysis results such as Ni 500 ppm, Cr 20000 ppm, Cu 250 ppm and Zn 300 ppm. This mixture of kiln feed should be used in equation 4.1 to predict the concentration of chromium in clinker after burning process. If the analysis of the sludge waste indicated that the concentration of heavy metals is almost similar (such as Ni 1100 ppm, Cr 1050 ppm, Cu 1120 ppm and Zn 950 ppm), then equation 4.2 should be selected to predict the concentration of chromium in clinker after burning process. If the analysis of the sludge waste was found that the concentration of heavy metals is totally different such as Ni 3000 ppm, Cr 9000 ppm, Cu 15000 ppm and Zn 21000 ppm, equation 4.3 should be used to predict the concentration of chromium in clinker.

4.2.1 The comparison of concentrations of Ni in kiln feed, clinker and cement mortar

Figure 4.4 and Table 4.6 shows the results obtained from total concentration of nickel in the kiln feed, the clinker and cement mortar were only added with nickel oxide. The result shows the amounts of Ni increased and detected from control, 1000, 5000, 10000, and 20000 ppm of initial concentrations of nickel doped in kiln feed from 25.73, 1125, 5216, 10231, and 19895 ppm respectively, whereas total concentration of nickel in clinker was increased to 39.34, 1964, 10586, 15795, and 29578 ppm respectively. However, total concentration of nickel in cement mortar was decreased to ND, 702, 3552, 4923, and 9525 ppm respectively. Because of cement mortar was mixed with sand, thus the concentration of nickel in cement was diluted. The result showed that the concentration of Ni was in the range of 1000 to 20000 ppm which it was not destroyed in burning process and occurred in clinker. However, the total concentration (TC) of Ni by Thai standard (DIW) must be less than 2000 mg/kg to be classified as non hazardous material. The concentration of Ni in the clinker and the cement mortar by WET could not be detected. The result showed that this concentration of Ni was not over Thai's standard (< 20 ppm).

Table 4.6: Analysis of the concentrations of Ni in the kiln feed, the clinker and the cement mortar.

Ratios of Ni (ppm)	Concentration of Ni by TC						Concentration of Ni by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	25.73	1.66	39.34	9.70	10.35	4.95	ND	ND
1000	1125	123.22	1964	48.54	702	43.86	ND	ND
5000	5216	99.95	10586	76.60	3552	52.16	ND	ND
10000	10231	29.31	15795	45.51	4923	52.05	ND	ND
20000	19895	67.27	29578	70.31	9525	62.43	ND	ND

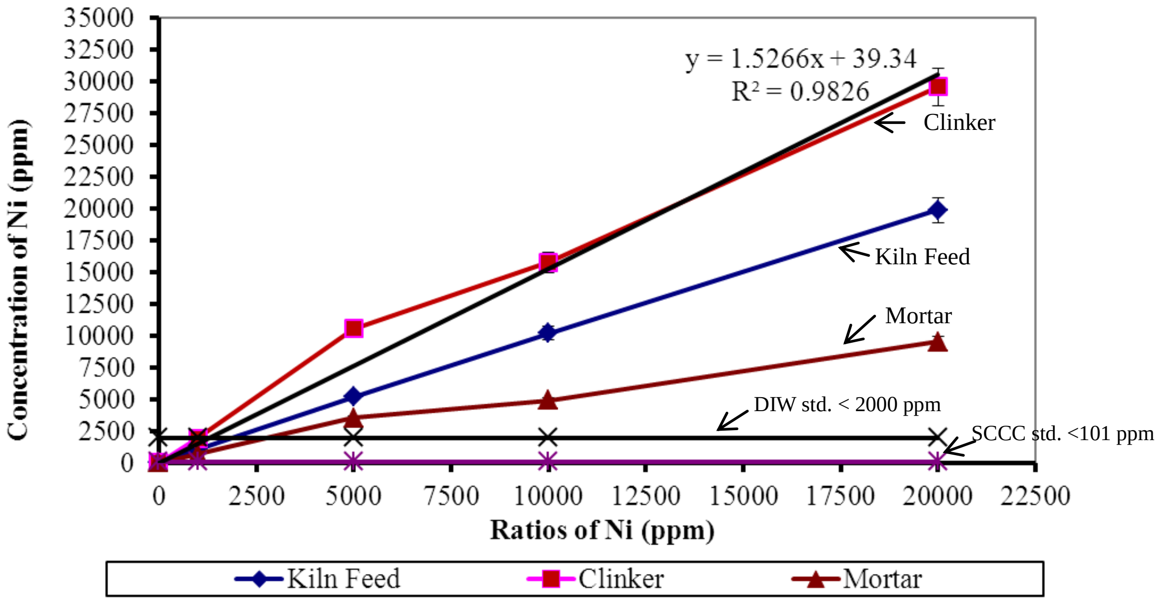


Figure 4.4: Comparison of the concentrations of Ni in the kiln feed, the clinker and the cement mortar

The comparison of the concentrations of Ni in combination of Ni:Cr:Cu:Zn = 1:1:1:1 in the kiln feed, the clinker and the cement mortar as shown in Table 4.7 and Figure 4.5. The results showed that the heavy metals were found in the clinker and cement mortar at different ratios. The amounts of Ni increased and detected of initial concentrations of Ni doped in kiln feed were in the range of 141 to 5312 ppm, whereas total concentration of nickel in clinker was increased in the range of 232 to 9175 ppm. However, total concentration of nickel in cement mortar was decreased in the range of 78 to 2354 ppm. Thus, Ni occurred in clinker and mortar and the concentration of Ni in the cement mortar less than in clinker because of mixing with sand. Nevertheless, we have to consider the total concentration (TC) of Ni by Thai standard (DIW) must be less than 2000 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of Ni in clinker at 101 ppm. The concentration of Ni in the clinker and the cement mortar by WET could not be detected which was not over Thai's standard (< 20 ppm).

Table 4.7: Analysis of the concentrations of Ni in combination of Ni:Cr:Cu:Zn =1:1:1:1 in the kiln feed, the clinker and the cement mortar.

Ratios of Ni (ppm)	Concentration of Ni by TC						Concentration of Ni by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	25.73	1.66	39.34	9.70	10.35	4.95	ND	ND
125	141	28.16	232	49.15	78.32	17.72	ND	ND
750	781	39.34	1125	28.79	375	34.39	ND	ND
1250	1279	54.62	1875	49.03	582	36.39	ND	ND
2500	2598	80.67	2976	55.43	952	71.55	ND	ND
5000	5312	108.67	9175	35.34	2354	72.23	ND	ND

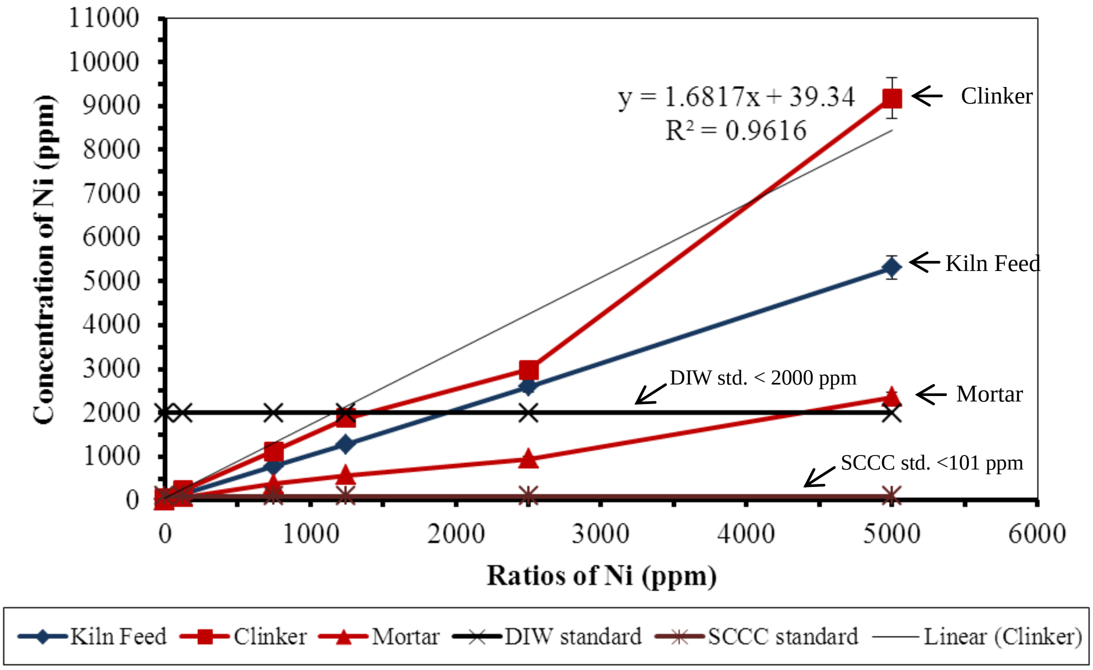


Figure 4.5: Comparison of the concentrations of Ni in combination of Ni:Cr:Cu:Zn = 1:1:1:1 in the kiln feed, the clinker and the cement mortar

The comparison of the concentrations of Ni in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar as shown in Table 4.8 and Figure 4.6. The results showed that the heavy metals were found in the clinker and cement mortar at different ratios. The amounts of Ni increased and detected of initial concentrations of Ni doped in kiln feed were in the range of 40.52 to 1320 ppm, whereas total concentration of nickel in clinker was increased in the range of 75.63 to 1724 ppm. However, total concentration of nickel in cement mortar was decreased in the range of 20.24 to 254 ppm. Therefore, Ni occurred in clinker and mortar and the concentration of Ni in the cement mortar less than in clinker because of mixing with sand. Nevertheless, we have to consider the total concentration (TC) of Ni by Thai standard (DIW) must be less than 2000 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of Ni in clinker at 101 ppm. The concentration of Ni in the clinker and the cement mortar by WET could not be detected which was not over Thai's standard (< 20 ppm).

Table 4.8: Analysis of the concentrations of Ni in combination of Ni:Cr:Cu:Zn =1:3:5:7 in the kiln feed, the clinker and the cement mortar.

Ratios of Ni (ppm)	Concentration of Ni by TC						Concentration of Ni by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	25.73	1.66	39.34	9.70	10.35	4.95	ND	ND
31.25	40.52	10.83	75.63	7.99	20.24	7.21	ND	ND
187.50	210	59.92	415	18.68	143	27.06	ND	ND
312.50	328	70.09	579	15.72	294	42.79	ND	ND
625.00	678	71.11	1023	61.25	352	50.48	ND	ND
1250.00	1320	60.22	1724	74.51	524	24.88	ND	ND

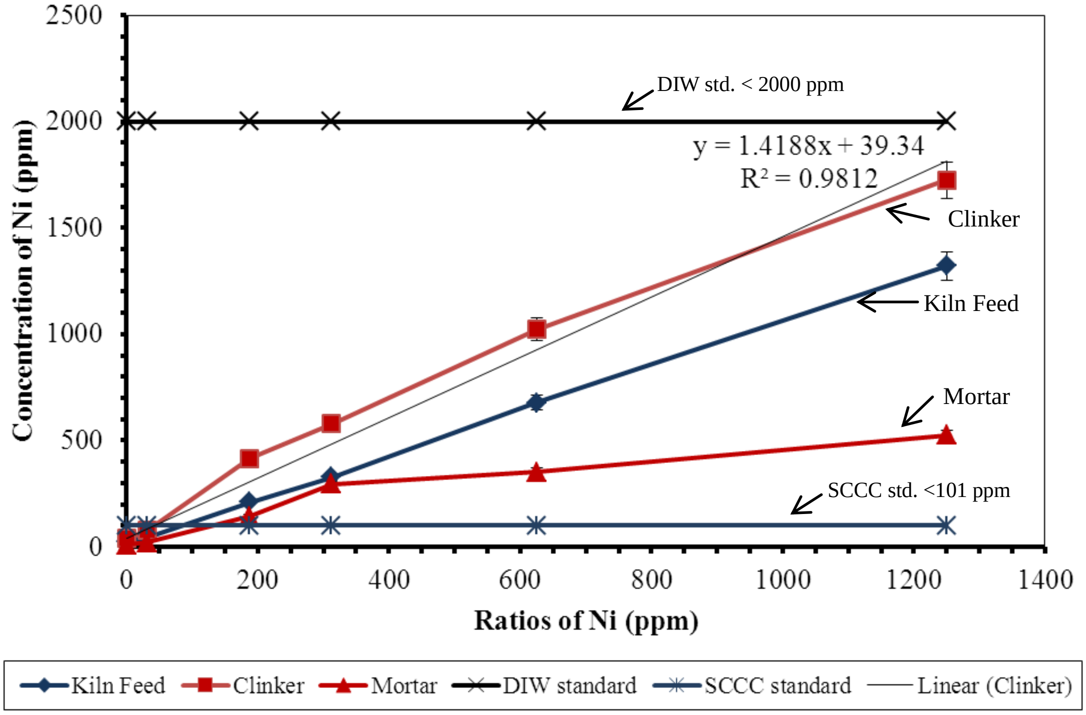


Figure 4.6: Comparison of the concentrations of Ni in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar

Therefore, nickel was not destroyed in burning process and occurred in clinker. Because of nickel is moderate volatile element (Kolovos et al., 2002), NiO_2 have high melting point and boiling point at 1455°C and 2730°C, respectively. Nickel oxides, when added to the clinker raw meal, do not evaporate during the burning process, at which 1% NiO, would not affect the emission ratio of these metals, even if the wastes have chlorides, and are thus incorporated into the clinker (Barros et al., 2002). The TC of nickel by Thai standard (DIW) must be less than 2000 mg/kg to be classified as non hazardous material. Thus, the total concentration of Ni in kiln feed must be added less than 1165 mg/kg when we use the equation 4.5 as shown below to predict the concentration of Ni in the clinker. Although, the standard of SCCC is normally control total concentration of nickel in clinker less than 101 ppm.

As the results, the linear equations in term of concentration of nickel (ppm or mg/kg) were prepared as shown below:

$$Y_{Ni} = 1.5266X_{Ni} + 39.34, \quad R^2 = 0.9826 \tag{4.4}$$

$$Y_{Ni} = 1.6817X_{Ni} + 39.34, \quad R^2 = 0.9616 \tag{4.5}$$

$$Y_{Ni} = 1.4188X_{Ni} + 39.34, \quad R^2 = 0.9812 \tag{4.6}$$

Whereas: Y_{Ni} = total concentration of Ni in clinker, ppm
X_{Ni} = total concentration of Ni added in kiln feed, ppm
39.34 = constant of initial concentration of Ni in clinker, ppm
R^2 shows linear equation which approaches 1.

Comparison of three equations as shown above was found to be similar to the linear equation because R^2 approached one. The slope of equation 4.5 was more than the others. The first equation (eq. 4.4) has a concentration of Ni in kiln feed greater than the others was in the range of 25.73 to 19895 ppm and the second equation (eq. 4.5) has concentration of Ni in kiln feed was in the range of 25.73 to 5312 ppm and the third equation (eq. 4.6) has concentration of Ni in kiln feed was in the range of 25.73 to 1320 ppm.

Thus, the equations 4.4 to 4.6 were used to predict the concentration of Ni in clinker to determine the concentration of Ni was added to the kiln feed and other heavy metals. The ratio that is similar or different which must be checked the suitable for predicting the initial concentration of Ni. If the raw material is only mixed with the sludge which high content of Ni, so it can be predicted from the range 25 to 20000 ppm by using eq. 4.4. The second equation (eq. 4.5) is suitable for predicting the concentration of Ni if the raw material is mixed with other heavy metals in same ratio which is similar to Ni:Cr:Cu:Zn = 1:1:1:1, which is predicted to range from 25 to 5300 ppm, and the third equation (eq. 4.6) is suitable for predicting the concentration of Ni if the raw material is mixed with other heavy metals in the ratios which is similar to Ni:Cr:Cu:Zn = 1:3:5:7, which is predicted to range from 25 to 1320 ppm. For example, when nickel sludge contained nickel higher than the other heavy metals which is shown from the analysis results, such as Ni 25000 ppm, Cr 500 ppm, Cu 200 ppm, Zn 200 ppm etc. This mixture of kiln feed should be used in equation 4.4 to predict the concentration of Ni in clinker after burning process. If the analysis result of the sludge waste indicated that the concentration of heavy metals is almost similar (such as Ni 900 ppm, Cr 850 ppm, Cu 720 ppm and Zn 700 ppm), then equation 4.5 should be selected to predict the concentration of Ni in clinker after burning process. If the analysis result of the sludge waste was found that the concentration of heavy metals is totally different such as Ni 2000 ppm, Cr 6000 ppm, Cu 10000 ppm and Zn 14000 ppm, equation 4.6 should be used to predict the concentration of Ni in clinker.

4.2.1 The comparison of concentrations of Cu in kiln feed, clinker and cement mortar

Figure 4.7 and Table 4.9 show the results obtained from total concentration of Copper (Cu) in the kiln feed, the clinker and cement mortar were added with Cu. The result shows the amounts of Cu increased and detected from control, 1000, 5000, 10000, and 20000 ppm of initial concentrations of Cu doped in kiln feed from 72.86, 987, 4985, 9953, and 19864 ppm respectively, whereas total concentration of Cu in clinker was increased to 130.94, 1945, 7683, 12146, and 29275 ppm respectively. However, total concentration of Cu in cement mortar was decreased from 10.25, 692, 2791, 4402, and 10451 ppm respectively, because cement mortar was mixed with sand, thus the concentration of Cu in cement was diluted. The result showed that the concentration of Cu was in the range of 1000 to 20000 ppm which it was not destroyed in burning process and occurred in clinker because of high melting and boiling point of Cu at 1084.62°C and 2562°C, respectively. The total concentration (TC) of Cu by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. The standard of SCCC is normally control total concentration of Cu in clinker less than 280 ppm. Although, the concentration of Cu in clinker by WET was increased in the range of 0.08 to 0.21 ppm, but it could not be detected in the cement mortar which was not over Thai’s standard (< 25 ppm).

Table 4.9: Analysis of the concentrations of Cu in the kiln feed, the clinker and the cement mortar.

Ratios of Cu (ppm)	Concentration of Cu by TC						Concentration of Cu by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	72.86	2.29	130.94	15.01	29.1	5.58	ND	ND
1000	987	118.90	1945	96.57	692	11.27	0.08	ND
5000	4985	98.23	7683	86.02	2791	16.82	0.11	ND
10000	9953	173.14	12146	102.94	4402	66.78	0.12	ND
20000	19864	197.41	29275	83.52	10451	65.00	0.21	ND

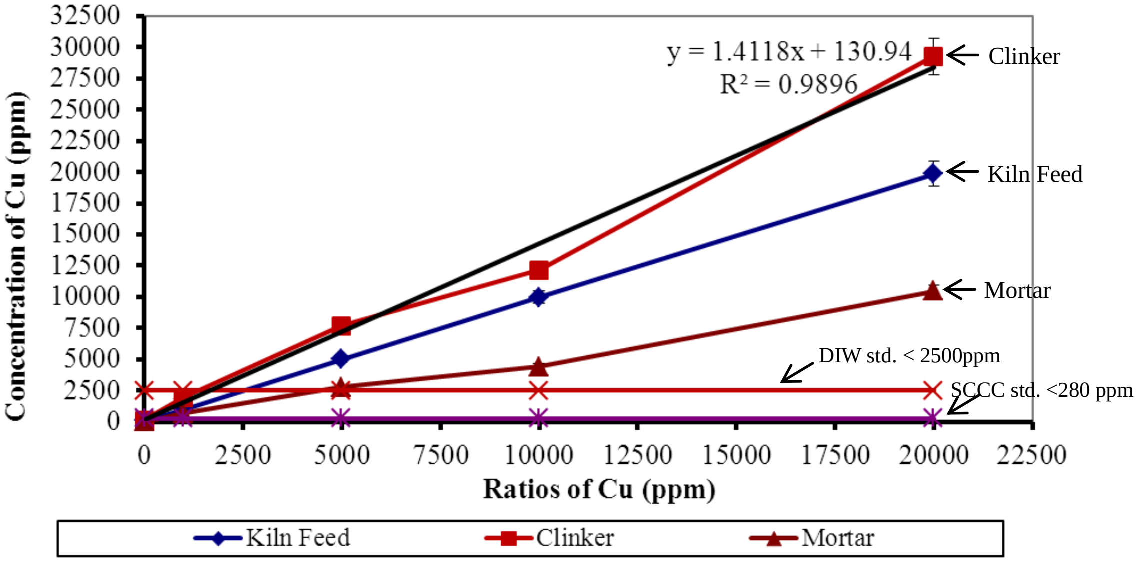


Figure 4.7: Comparison of the concentrations of Cu in the kiln feed, the clinker and the cement mortar

Considering the concentrations of Cu in combination of Ni:Cr:Cu:Zn = 1:1:1:1 in the kiln feed, the clinker and the cement mortar as shown in Table 4.10 and Figure 4.8. The results showed that the heavy metals were found in the clinker and cement mortar at different ratios. The amounts of Cu increased and detected of initial concentrations of Cu doped in kiln feed were in the range of 189 to 5025 ppm, whereas total concentration of Cu in clinker was increased in the range of 268 to 5280 ppm. However, total concentration of Cu in cement mortar was decreased in the range of 81 to 1611 ppm. Because of cement mortar was mixed with sand which the concentration of Cu in cement was diluted. Thus, Cu occurred in clinker and mortar, so we have to consider the total concentration (TC) of Cu by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of Cu in clinker at 280 ppm. Although, the concentration of Cu in clinker by WET was increased in the range of 0.35 to 0.81 ppm, but it could not be detected in the cement mortar which was not over Thai’s standard (< 25 ppm).

Table 4.10: Analysis of the concentrations of Cu in combination of Ni:Cr:Cu:Zn =1:1:1:1 in the kiln feed, the clinker and the cement mortar.

Ratios of Cu (ppm)	Concentration of Cu by TC						Concentration of Cu by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	72.86	2.29	130.94	15.01	29.1	5.58	ND	ND
125	189	12.12	268	36.59	81.23	16.35	ND	ND
750	715	67.67	774	45.21	437	24.33	0.35	ND
1250	1221	86.03	1254	64.82	437	43.27	0.48	ND
2500	2561	89.71	2746	73.12	852	47.89	0.52	ND
5000	5025	112.62	5280	38.35	1611	24.52	0.81	ND

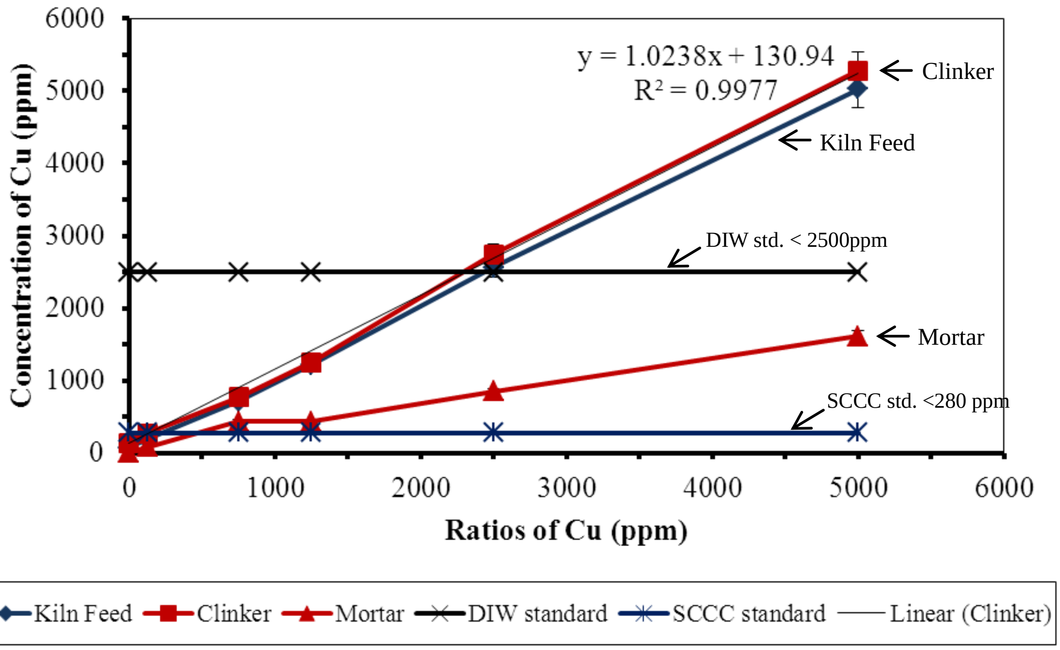


Figure 4.8: Comparison of the concentrations of Cu in combination of Ni:Cr:Cu:Zn = 1:1:1:1 in the kiln feed, the clinker and the cement mortar

Considering the concentrations of Cu in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar as shown in Table 4.11 and Figure 4.9. The results showed that the heavy metals were found in the clinker and cement mortar at different ratios. The amounts of Cu increased and detected of initial concentrations of Cu doped in kiln feed were in the range of 218 to 6250 ppm, whereas total concentration of Cu in clinker was increased in the range of 292 to 6435 ppm. However, total concentration of Cu in cement mortar was decreased in the range of 98 to 2058 ppm. Because of cement mortar was mixed with sand which the concentration of Cu in cement was diluted. Thus, Cu was trapped in clinker and mortar, so we have to consider the total concentration (TC) of Cu by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of Cu in clinker at 280 ppm. Although, the concentration of Cu in clinker by WET was increased in the range of 0.38 to 0.92 ppm, but it could not be detected in the cement mortar and it was not over Thai's standard (< 25 ppm).

Table 4.11: Analysis of the concentrations of Cu in combination of Ni:Cr:Cu:Zn =1:3:5:7 in the kiln feed, the clinker and the cement mortar.

Ratios of Cu (ppm)	Concentration of Cu by TC						Concentration of Cu by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	72.86	2.29	130.94	15.01	29.1	5.58	ND	ND
156.25	218	46.87	292	17.44	98.35	17.02	ND	ND
937.50	1014	115.47	1268	48.51	409	41.80	0.38	ND
1562.50	1558	58.03	1695	24.58	567	38.43	0.42	ND
3125.00	2514	59.92	2954	57.56	1168	15.10	0.52	ND
6250.00	6358	61.00	6435	48.12	2058	43.58	0.92	ND

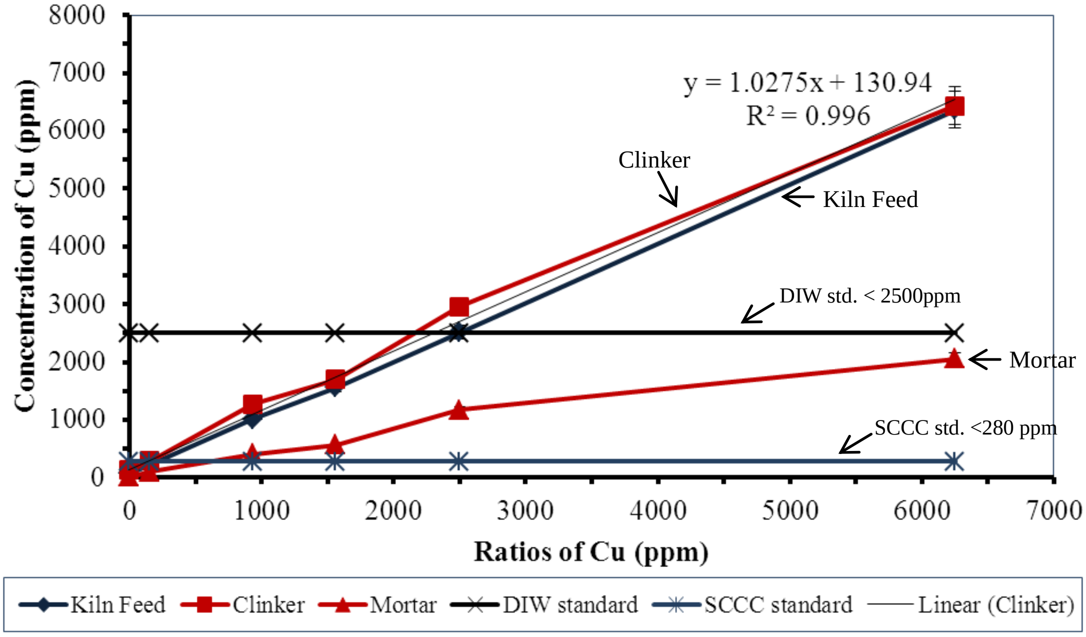


Figure 4.9: Comparison of the concentrations of Cu in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar

The results showed that Cu was not destroyed in burning process and occurred in clinker. Because of high of melting point and boiling point of Cu at 1084.62°C and 2562°C, respectively. The same results of previous research led to the conclusion that additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.% Cu and 1.2 wt.% Ni to clinker raw-material do not affect the clinkering reactions and that these metals are totally incorporated into the clinker (Ract et al., 2003). The TC of Cu by Thai standard (DIW) must be less than 2500 mg/kg to be classified as non hazardous material. Thus, the total concentration of Cu in kiln feed must be less than 1678 mg/kg when we use the equation 4.7 as shown below to predict the concentration of Cu in the clinker. Although, the standard of SCCC is normally to control total concentration of chromium in clinker at 280 ppm to control the qualities of cement products.

As the results, The linear equation in term of concentration of copper (ppm or mg/kg) was prepared as shown below:

$$Y_{Cu} = 1.4118X_{Cu} + 130.94, \quad R^2 = 0.9896 \qquad (4.7)$$

$$Y_{Cu} = 1.0238X_{Cu} + 130.94, \quad R^2 = 0.9877 \qquad (4.8)$$

$$Y_{Cu} = 1.0275X_{Cu} + 130.94, \quad R^2 = 0.9960 \qquad (4.9)$$

Whereas: $\mathbf{Y_{Cu}}$ = total concentration of Cu in clinker, ppm

$\mathbf{X_{Cu}}$ = total concentration of Cu added in kiln feed, ppm

130.94 = constant of initial concentration of Cu in clinker, ppm

R^2 shows linear equation which approaches 1.

Comparison of three equations as shown above was found to be similar to the linear equation because R^2 approached one. The slope of equation 4.7 was more than the others. The first equation (eq. 4.7) has a concentration of Cu in kiln feed greater than the others was in the range of 72 to 20000 ppm and the second equation (eq. 4.8) has concentration of Cu in kiln feed was in the range of 72 to 5025 ppm and the third equation (eq. 4.9) has concentration of Cu in kiln feed was in the range of 72 to 6358 ppm. Thus, it can be used to predict the concentration of Cu in clinker to determine the concentration of Cu was added to the kiln feed and other heavy metals. The ratio that is similar or different which must be checked the suitable for predicting the initial concentration of Cu. If the raw material is only mixed with the sludge which high content of Cu, so it can be predicted from the range 72 to 20000 ppm by using eq. 4.7. The second equation (eq. 4.8) is suitable for predicting the concentration of Cu if the raw material is mixed with other heavy metals in same ratio which is similar to Ni:Cr:Cu:Zn = 1:1:1:1, which is predicted to range from 72 to 5300 ppm, and the third equation (eq. 4.9) is suitable for predicting the concentration of Cu if the raw material is mixed with other heavy metals in the ratios which is different ratio to be Ni:Cr:Cu:Zn = 1:3:5:7, which is predicted to range from 72 to 6250 ppm. For example, when copper sludge contained copper higher than the other heavy metals which is shown from the analysis results, such as Ni 200 ppm, Cr 250 ppm, Cu 20000 ppm, Zn 200 ppm etc. This mixture of kiln feed should be used in equation 4.7 to predict the concentration of Cu in clinker after burning process. If the analysis result of the sludge waste indicated that the concentration of heavy metals is almost similar (such as Ni 500 ppm, Cr 550 ppm, Cu 520 ppm and Zn 510 ppm), then equation 4.8 should be selected to predict the concentration of Cu in clinker after burning process. If the analysis result of the sludge waste was found that the concentration of heavy metals is totally different such as Ni 1000 ppm, Cr 3000 ppm, Cu 5000 ppm and Zn 7000 ppm, equation 4.9 should be used to predict the concentration of Cu in clinker.

4.2.1 The comparison of concentrations of Zn in kiln feed, clinker and cement mortar

Figure 4.10 and Table 4.12 show the results obtained from total concentration of Zinc (Zn) in the kiln feed, the clinker and cement mortar were added with Zn. The result shows the amounts of Zn increased and detected from control, 1000, 5000, 10000, and 20000 ppm of initial concentrations of Zn doped in kiln feed from 157.43, 1285, 5148, 10171, and 19952 ppm respectively, whereas total concentration of Zn in clinker was increased to 229.56, 1455, 5738, 10303, and 21091 ppm respectively. However, total concentration of Zn in cement mortar was decreased from 15.12, 443, 1793, 2941, and 6202 ppm respectively, because cement mortar was mixed with sand, thus the concentration of Zn in cement was diluted. The result showed that the concentration of Zn was in the range of 157 to 20000 ppm which it was not destroyed in burning process and occurred in clinker. However, the total concentration (TC) of Zn by Thai standard (DIW) must be less than 5000 mg/kg to be classified as non hazardous material. The concentration of Zn in clinker by WET was increased in the range of 0.20 to 0.41 ppm, but it could not be detected in the cement mortar. The result showed that this concentration of Zn was still in the range of Thai's standard (< 250 ppm). The standard of SCCC is normally control total concentration of Zn in clinker less than 370 ppm.

Table 4.12: Analysis of the concentrations of Zn in the kiln feed, the clinker and the cement mortar.

Ratios of Zn (ppm)	Concentration of Zn by TC						Concentration of Zn by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	157.43	4.62	229.56	95.54	45.91	10.83	ND	ND
1000	1285	30.64	1455	102.37	443	63.98	0.20	ND
5000	5148	19.31	5738	81.66	1793	16.52	0.25	ND
10000	10171	12.29	10303	118.20	2941	51.39	0.29	ND
20000	19952	30.45	21091	73.43	6202	49.52	0.41	ND

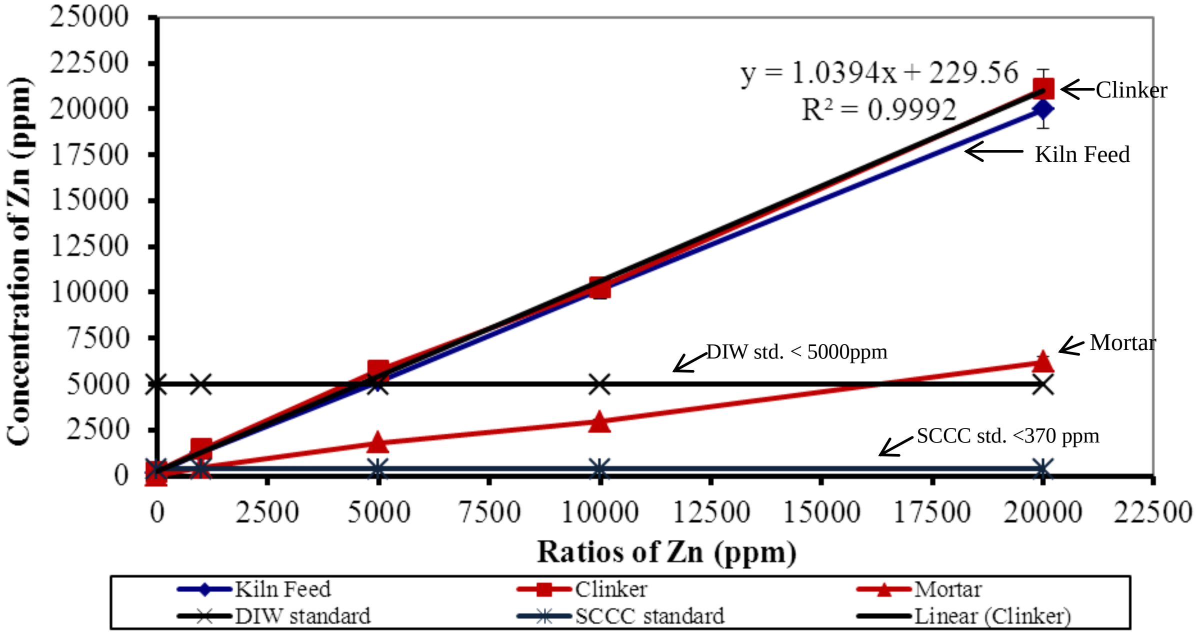


Figure 4.10: Comparison of the concentrations of Zn in the kiln feed, the clinker and the cement mortar

Moreover, Table 4.13 and Figure 4.11 gives the initial concentrations of Zn doped in kiln feed were in the range of 265 to 5254 ppm, whereas total concentration of Zn in clinker was increased in the range of 299 to 5621 ppm, respectively. However, total concentration of Zn in cement mortar was decreased in the range of 85 to 1606 ppm. Because cement mortar was mixed with sand, the concentration of Zn in cement was diluted. The result showed that the concentration of Zn was in the range of 72 to 5254 ppm which it was not destroyed in burning process and occurred in clinker. However, the total concentration (TC) of Zn by Thai standard (DIW) must be less than 5000 mg/kg to be classified as non hazardous material. The concentration of Zn in clinker by WET was increased in the range of 0.11 to 0.27 ppm, but it could not be detected in the cement mortar. The result showed that this concentration of Zn was still in the range of of Thai's standard (< 250 ppm). The standard of SCCC is normally to control total concentration of Zn in clinker less than 370 ppm.

Table 4.13: Analysis of the concentrations of Zn in combination of Ni:Cr:Cu:Zn =1:1:1:1 in the kiln feed, the clinker and the cement mortar.

Ratios of Zn (ppm)	Concentration of Zn by TC						Concentration of Zn by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	72.86	2.29	130.94	15.01	29.1	5.58	ND	ND
125	265	9.64	299	319	85.14	8.83	ND	ND
750	889	20.42	916	1375	429	24.56	0.11	ND
1250	1468	68.64	1465	1918	485	15.72	0.12	ND
2500	2675	67.73	2708	3176	820	31.61	0.15	ND
5000	5254	118.49	5621	7498	1606	65.96	0.27	ND

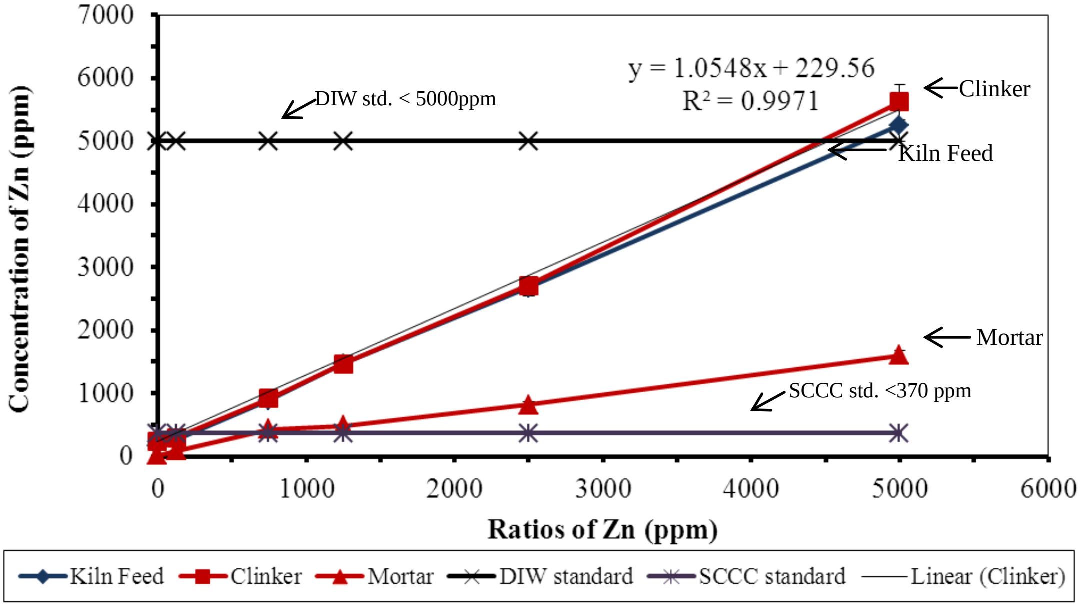


Figure 4.11: Comparison of the concentrations of Zn in combination of Ni:Cr:Cu:Zn = 1:1:1:1 in the kiln feed, the clinker and the cement mortar

Considering the concentrations of Zn in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar as shown in Table 4.14 and Figure 4.12. The results showed that the heavy metals were found in the clinker and cement mortar at different ratios. The amounts of Zn increased and detected of initial concentrations of Zn doped in kiln feed were in the range of 315 to 8824 ppm, whereas total concentration of Zn in clinker was increased in the range of 390 to 9126 ppm. However, total concentration of Zn in cement mortar was decreased in the range of 117 to 2935 ppm. Because of cement mortar was mixed with sand which the concentration of Cu in cement was diluted. Thus, Zn was trapped in clinker and mortar, so we have to consider the total concentration (TC) of Zn by Thai standard (DIW) must be less than 5000 mg/kg to be classified as non hazardous material. The standard of SCCC is normally to control total concentration of Zn in clinker at 370 ppm. Although, the concentration of Zn in clinker by WET was increased in the range of 0.10 to 0.38 ppm, but it could not be detected in the cement mortar and it was not over Thai's standard (< 250 ppm).

Table 4.14: Analysis of the concentrations of Zn in combination of Ni:Cr:Cu:Zn =1:3:5:7 in the kiln feed, the clinker and the cement mortar.

Ratios of Zn (ppm)	Concentration of Zn by TC						Concentration of Zn by WET	
	Kiln Feed (ppm)	SD	Clinker (ppm)	SD	Mortar (ppm)	SD	Clinker (ppm)	Mortar (ppm)
Control	72.86	2.29	130.94	15.01	29.1	5.58	ND	ND
218.75	315	68.64	390	207	117	10.82	ND	ND
1312.50	1464	69.54	1505	982	442	36.06	0.10	ND
2187.50	2285	30.35	2323	1797	741	22.27	0.14	ND
4375.00	4436	136.86	4536	2812	2478	77.74	0.20	ND
8750.00	8824	78.62	9126	4905	2935	41.33	0.38	ND

Therefore, Zn was not destroyed in burning process and occurred in clinker. Because Zn is moderate volatile element, melting point and boiling point at 419°C and 907°C respectively; however, zinc oxide (ZnO) has the melting point at 1975°C. Among the added metals, Zn is more easily incorporated in C_3S, followed by V and Pb (Andrade et al., 2003). The total concentration (TC) of Zn by Thai standard (DIW) must be less than 5000 mg/kg to be classified as non hazardous material. Thus, the total concentration of Zn in kiln feed must be less than 4522 mg/kg when we use the equation 4.11 to predict the concentration in the clinker. Although, the standard of SCCC is normally control total concentration of Zn in clinker less than 370 ppm.

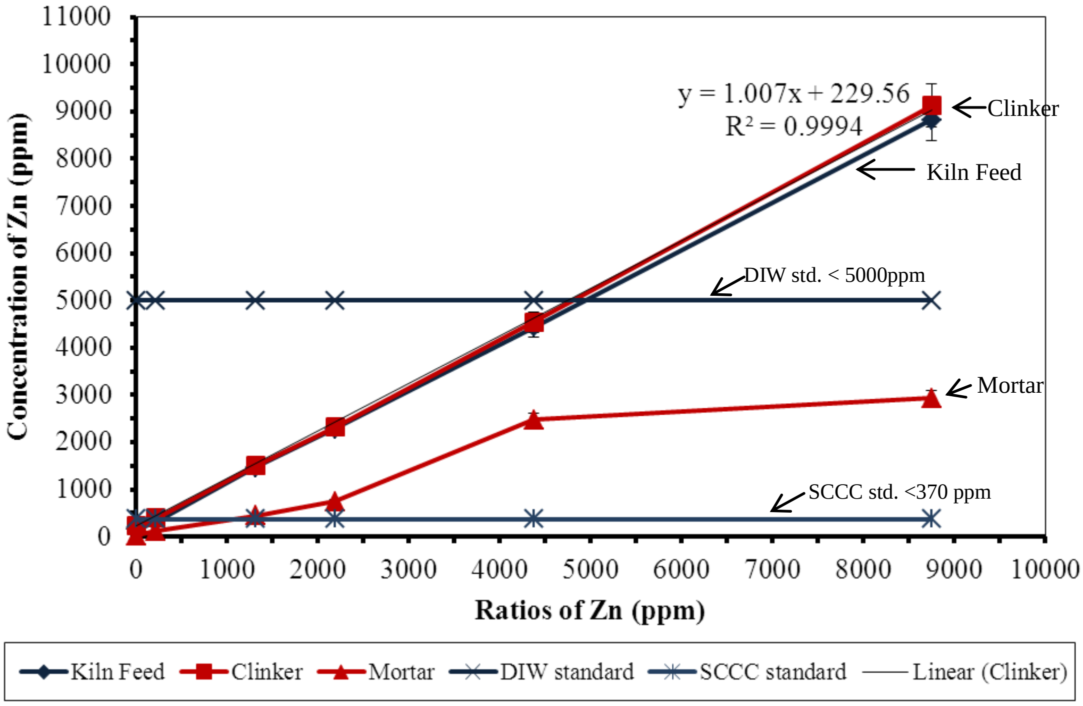


Figure 4.12: Comparison of the concentrations of Zn in combination of Ni:Cr:Cu:Zn = 1:3:5:7 in the kiln feed, the clinker and the cement mortar

As the results, the linear equations in term of concentration of zinc (ppm or mg/kg) was prepared as shown in below;

$$Y_{Zn} = 1.0394X_{Zn} + 229.56, \quad R^2 = 0.9992 \quad (4.10)$$

$$Y_{Zn} = 1.0548X_{Zn} + 229.56, \quad R^2 = 0.9971 \quad (4.11)$$

$$Y_{Zn} = 1.007X_{Zn} + 229.56, \quad R^2 = 0.9994 \quad (4.12)$$

Whereas: $\mathbf{Y_{Zn}}$ = total concentration of Zn in clinker, mg/kg

$\mathbf{X_{Zn}}$ = total concentration of Zn added in kiln feed, mg/kg

229.56 = constant of initial concentration of Zn in clinker, ppm

R^2 shows linear equation which approaches 1.

Comparison of three equations as shown above was found to be similar to the linear equation because R^2 approached one. The slope of equation 4.11 was more than the others. The first equation (eq. 4.10) has a concentration of Zn in kiln feed greater than the others was in the range of 72 to 20000 ppm and the second equation (eq.

4.11) has concentration of Zn in kiln feed was in the range of 72 to 5254 ppm and the third equation (eq. 4.12) has concentration of Zn in kiln feed was in the range of 72 to 8824 ppm. Thus, it can be used to predict the concentration of Zn in clinker to determine the concentration of Zn was added to the kiln feed and other heavy metals. The ratio that is similar or different which must be checked the suitable for predicting the initial concentration of Zn. If the raw material is only mixed with the sludge which high content of Zn, so it can be predicted from the range 72 to 20000 ppm by using eq. 4.10. The second equation (eq. 4.11) is suitable for predicting the concentration of Zn if the raw material is mixed with other heavy metals in same ratio which is similar to Ni:Cr:Cu:Zn = 1:1:1:1, which is predicted to range from 72 to 5254 ppm, and the third equation (eq. 4.12) is suitable for predicting the concentration of Zn if the raw material is mixed with other heavy metals in the ratios which is different ratio to be Ni:Cr:Cu:Zn = 1:3:5:7, which is predicted to range from 72 to 8824 ppm. For example, when zinc sludge is containing Zn higher than the other heavy metals which is shown from the analysis results, such as Ni 200 ppm, Cr 250 ppm, Cu 200 ppm, Zn 20000 ppm etc. This mixture of kiln feed should be used in equation 4.10 to predict the concentration of Zn in clinker after burning process. If the analysis result of the sludge waste indicated that the concentration of heavy metals is almost similar (such as Ni 400 ppm, Cr 450 ppm, Cu 420 ppm and Zn 410 ppm), then equation 4.11 should be selected to predict the concentration of Zn in clinker after burning process. If the analysis result of the sludge waste was found that the concentration of heavy metals is totally different such as Ni 3000 ppm, Cr 9000 ppm, Cu 15000 ppm and Zn 21000 ppm, equation 4.12 should be used to predict the concentration of Zn in clinker.

4.3 The chemical composition of clinker at different ratios of heavy metals

4.3.1 The content of free lime

The free lime is the first indicator of burning process because of low percentage of free lime (lower than 1.5%) means an improvement ability of burning process and complete form in the clinker product. However, high concentration of free lime indicated deterioration in the burning process, inactive produced clinker, and easily broken clinker. Thus, the standard of SCCC is normally to control the free lime content in clinker lower than 1.5%.

The percent concentration of free lime was increased when the Cr concentration in the clinker increased to 2.0 %wt. as shown in Table 4.15 and Figure 4.13. The result showed the free lime content at different ratios of chromium concentrations less than 0.5 wt.% (according to the total weight of sample), the free lime content was gradually increased in the range from 0.78% to 1.26%. On the other hand, high concentration of 1.0-2.0 wt.% of chromium, the content of free lime was increased in the range of 2.22-2.82% which was over standard limit at 1.5% of free lime. The results showed that the Cr content increased which has affected the reactivity of the C_3S by inhibiting interactions between C_2S and CaO to form C_3S. Some effects of the chromium on the free lime content in clinker were described by previous researchers. Taweekitwanit (2004) found a concentration of free lime was increased by 1.21% to 4.0% when doped with chromium between 0.5 to 2 wt.% respectively. Stephan et al (1999) found a concentration of 0.5 wt.% of chromium, the content of free lime decreased. Between 0.5 and 2.5 wt.%, the doping with chromium led to a high concentration of free lime, so Cr affected the formation of clinker phases. Malozhon et al. (1971) also found the same results a concentration of 1.5 wt.% of Cr_2O_3 in the sample, the content of free lime rose extremely. Thus, high concentration of Cr has measurable effects on the formation and composition of clinker.

Table 4.15: Comparison of free lime between in the clinker control and in clinker samples with different ratios of Cr.

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Cr: 1000 (0.1% by weight)	1.260
Cr: 5000 (0.5% by weight)	1.120
Cr: 10000 (1.0% by weight)	2.820
Cr: 20000 (2.0% by weight)	2.220

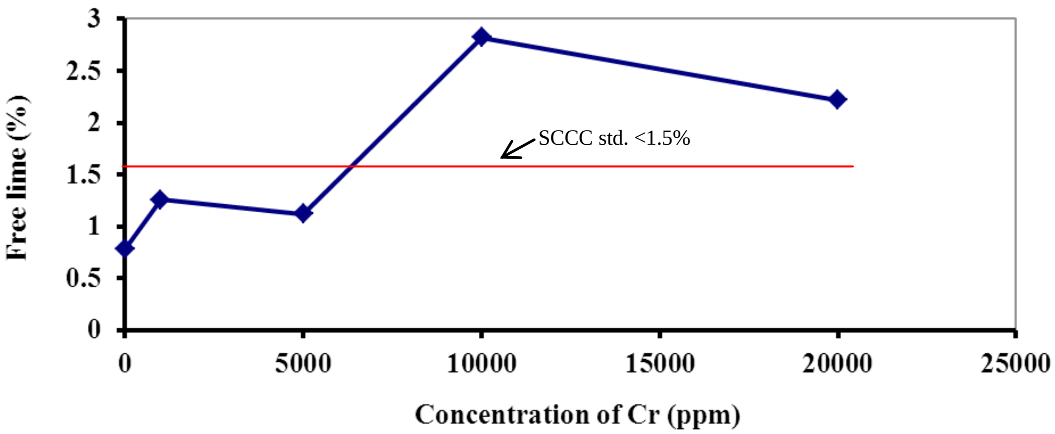


Figure 4.13: Percent free lime in the clinker with different ratios of Cr

Table 4.16 and Figure 4.14 showed the percent concentration of free lime was slightly increased when the Ni concentration increased in kiln feed from 0.1 up to 2.0 % wt. The percent concentration of free lime was gradually increased in the clinker from ratio of Ni are 0.50, 0.77, 0.60 and 1.00 % were the percent free lime of clinker from the Ni ratios at 0.1, 0.5, 1.0 and 2.0% wt., respectively. Although, the highest concentration of Ni was 2.0% wt. the free lime content was slightly increased, but it was not over 1.5%. Because the standard of SCCC is normally to control the free lime content in clinker to be less than 1.5%, thus the increased concentration of Ni had no effect to free lime content which reduced the free lime content in the clinker as same as the previous studies found that high concentration of Ni can reduce the concentration of free lime in clinker product (Stephan et al,1999a; Taweekitwanit,2004)

Table 4.16: Comparison of free lime in the clinker control between clinker samples with different ratios of Ni.

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Ni: 1000 (0.1% by weight)	0.500
Ni: 5000 (0.5% by weight)	0.770
Ni: 10000 (1.0% by weight)	0.600
Ni: 20000 (2.0% by weight)	1.000

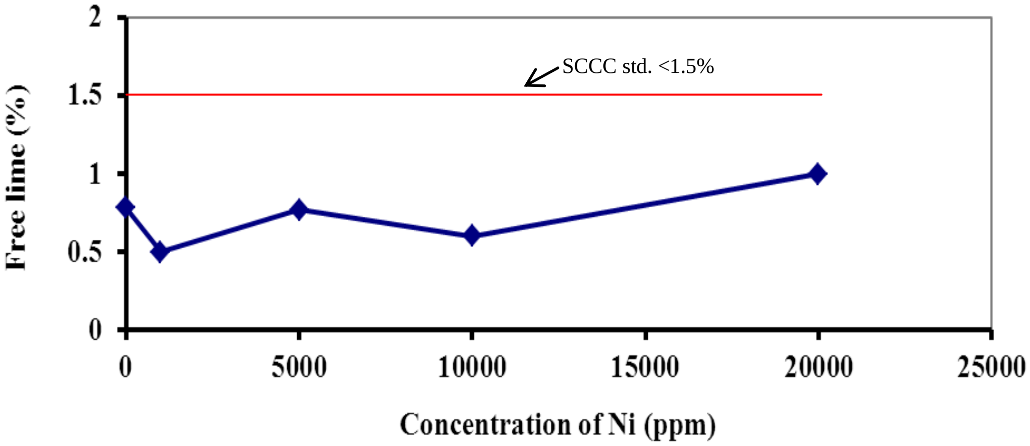


Figure 4.14: Percent free lime in the clinker with different ratios of Ni

At the different ratios of Cu in the clinker, the results were shown in Table 4.17 and Figure 4.15. The percent concentration of free lime was rose extremely when the Cu concentration increased in kiln feed from 0.1 up to 2.0 % wt. The percent concentration of free lime was extremely increased in the clinker from ratio of Cu are 0.78, 1.16, 11.46 and 12.70 % resulting in the percent free lime of clinker from the Cu ratio at 0.1, 0.5, 1.0 and 2.0% by wt., respectively. However, the concentration of Cu more than 1.0% by wt. caused to the free lime content over 1.5% which inactive produced clinker, and easily broken clinker. The results showed that high concentration of Cu had affected for inhibiting the reaction between C_2S and CaO to form C_3S which are the composition of clinker and Kakali et al (1996) found that the CuO has promoted the combination of free lime in the clinker as well as C_3S and C_2S can be produced at low temperature such as 1300°C.

Table 4.17: Comparison of free lime between in the clinker control and in clinker samples with different ratios of Cu

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Cu: 1000 (0.1% by weight)	0.780
Cu: 5000 (0.5% by weight)	1.160
Cu: 10000 (1.0% by weight)	11.460
Cu: 20000 (2.0% by weight)	12.700

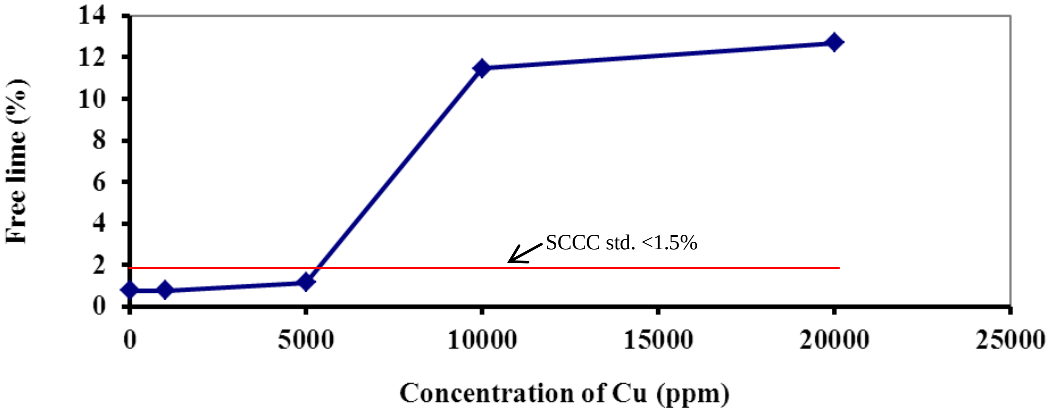


Figure 4.15: Percent free lime in the clinker with different ratios of Cu

At the different ratios of the concentration of Zn which added in the kiln feed, the result showed that the percent free lime in the clinker was slightly decreased when increasing concentration of Zn in the clinker. At the 0.1, 0.5, 1.0, and 2.0 % wt. of Zn, percent free lime in clinker was 0.890, 0.780, 0.830, and 0.830%, respectively as shown in Table 4.18 and Figure 4.16. Although, the highest concentration of Zn was 2.0% wt. the free lime content was not over 1.5%. Thus, the increased concentration of Zn had no effect to free lime content which reduced the free lime content in the clinker as same as the previous studies found that high concentration of Zn can reduced the free lime content in clinker product and improve the burnability of kiln feed (Stephan et al, 1999a; Taweekitwanit, 2004; Knofel et al, 1978; Older et al, 1980).

Table 4.18: Comparison of free lime between in the clinker control and in clinker samples with different ratios of Zn

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Zn: 1000 (0.1% by weight)	0.890
Zn: 5000 (0.5% by weight)	0.780
Zn: 10000 (1.0% by weight)	0.830
Zn: 20000 (2.0% by weight)	0.830

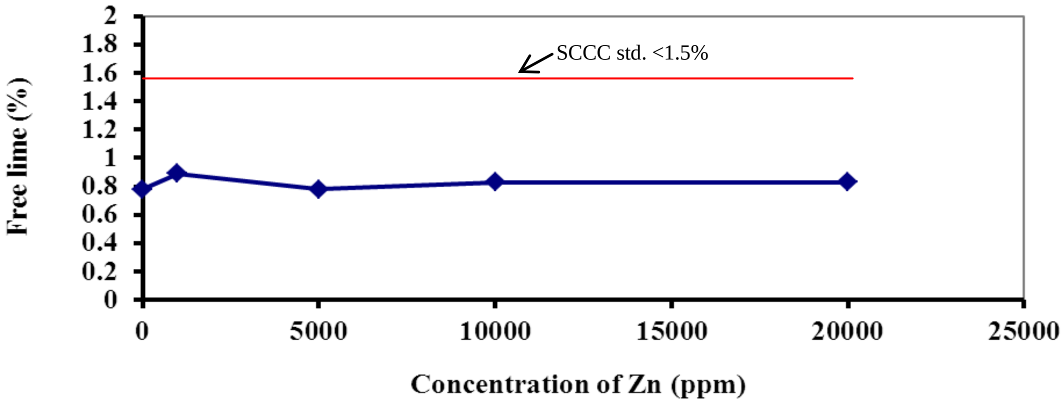


Figure 4.16: Percent free lime in the clinker with different ratios of Zn

Table 4.19 and Figure 4.17 showed the percent concentration of free lime was increased when the different ratios of combination of Ni:Cr:Cu:Zn =1:1:1:1 increased in kiln feed from 0.05 up to 2.0% wt. The percent concentration of free lime was gradually increased at the clinker from ratio of combination of Ni:Cr:Cu:Zn were in the range of 0.660 to 1.210%. Although, the highest concentration of combination ratio is 2.0% wt. but the free lime content was not over 1.5%. The results showed that at concentrations greater than 1.0 – 2.0% wt., the free lime content increased because the concentration of Cr and Cu increased from 2500 to 5000 ppm, which affects the free lime content as mentioned above.

Table 4.19: Comparison of free lime between in the clinker control and in clinker samples combination of Ni:Cr:Cu:Zn =1:1:1:1

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Ni:Cr:Cu:Zn (125:125:125:125) = 500ppm	0.660
Ni:Cr:Cu:Zn (750:750:750:750) = 3000ppm	0.880
Ni:Cr:Cu:Zn (1250:1250:1250:1250) = 5000ppm	0.720
Ni:Cr:Cu:Zn (2500:2500:2500:2500) = 10000ppm	0.670
Ni:Cr:Cu:Zn (5000:5000:5000:5000) = 20000ppm	1.210

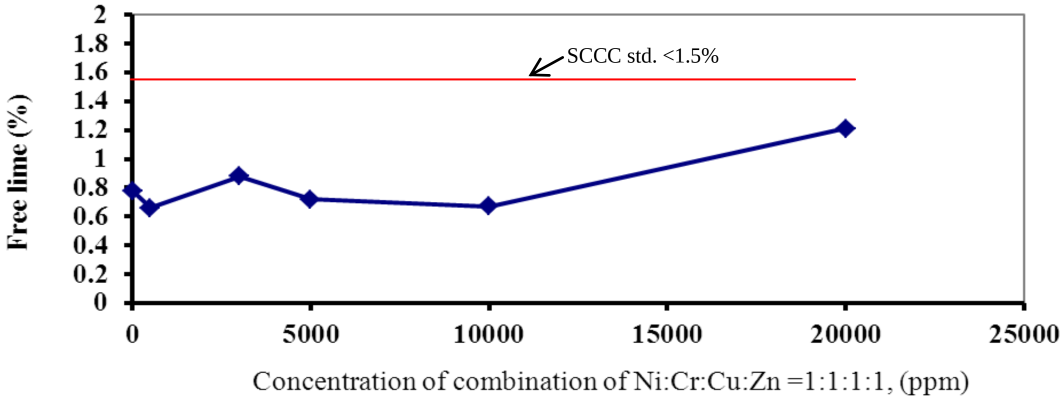


Figure 4.17: Percent free lime in the clinker with different ratios of combination of Ni:Cr:Cu:Zn =1:1:1:1

Table 4.20 and Figure 4.18 showed the percent concentration of free lime was decreased when the different ratios of combination of Ni:Cr:Cu:Zn =1:3:5:7 increased in kiln feed from 0.05 up to 1.0% wt. The percent concentration of free lime was gradually decreased at the clinker from ratio of combination of Ni:Cr:Cu:Zn were in the range of 0.78 to 0.61%. When the concentrations of heavy metals were over than 1 - 2% wt. the free lime content increased, and the highest concentration of combination ratio is 2.0% wt. the free lime was increased to 1.920% which was over the standard 1.5% because of the concentration of Cr increased from 1875 to 3750 ppm, and especially Cu increased from 2500 to 6250 ppm which have affected the free lime content as mentioned above.

Table 4.20: Comparison of free lime between in the clinker control and in clinker samples combination of Ni:Cr:Cu:Zn =1:3:5:7

Sample (ppm)	Free CaO (%)
Clinker from manufacturing	0.660
Control	0.780
Ni:Cr:Cu:Zn (31.25/93.75/156.25/218.75) = 500ppm	0.720
Ni:Cr:Cu:Zn (187.50/562.50/937.50/1312.50) = 3000ppm	0.660
Ni:Cr:Cu:Zn (312.5/937.5/1562.5/2187.50) = 5000ppm	0.610
Ni:Cr:Cu:Zn (625/1875/2500/4375) = 10000ppm	0.620
Ni:Cr:Cu:Zn (1250/3750/6250/8750) = 20000ppm	1.92

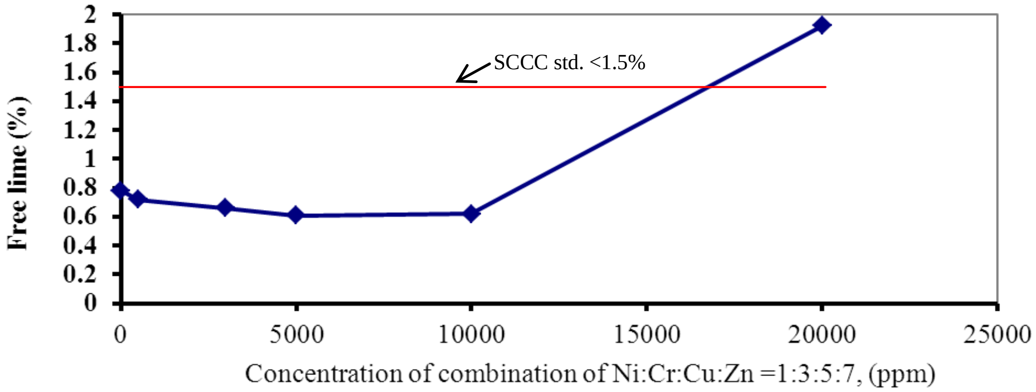


Figure 4.18: Percent free lime in the clinker with different ratios of combination of Ni:Cr:Cu:Zn =1:3:5:7

The results showed that high concentration of Cr and Cu had affected on inhibiting the reaction between C_2S and CaO to form C_3S which are the composition of clinker, so the free lime content increased over than the standard; however, high concentration of Ni and Zn decreased the free lime content lower than 1.5% . Kakali et al (1996) found that the CuO has promoted the combination of free lime in the clinker as well as C_3S and C_2S can be produced at low temperature such as 1300°C. Malozhon et al (1971) found that the concentration of 1.5 wt.% of Cr_2O_3 in the sample, the content of free lime was extremely increased. Some effects of heavy metals to clinker was found high concentration of Ni and Zn can permanently reduce concentration of free lime in clinker and improve burning ability of kiln feed (Stephan et al., 1999a; Knofel et al., 1978). However, at 2.5 wt% of Cr was increased free lime content in the clinker around 3.2% (Odler and Schmidt, 1980). Taweekitwanit (2004) found the free lime increased to 4.005% at 2 wt% of Cr; whereas, the increased concentration of Ni and Zn reduced free lime content in the clinker product. 2.0 wt% of Ni in the kiln feed sample gave 0.64% of free lime content of clinker. 2.0 wt% of Zn in the kiln feed sample gave 0.365% of free lime content of clinker.

4.3.2 The content of chemical oxides and chemical compounds in the clinker

The instrument which combined of XRF and XRD was used to analyze concentration of chemical oxides and chemical compounds inside the control kiln feed and mixtures. Chemical minerals and chemical oxides indicated the setting form of clinker whereas LSF, SM, and AM related to burning process and strength of cement. Suitable values were given complete in burning process. The XRF was used to analyze concentration of chemical oxide which calculated from the oxide analyses as shown in eq. 2.6 to 2.7. The XRD was used to verify the identity of the chemical compounds inside the clinker due to the samples were not destroyed (Non-destructive method) on the basis of X-ray diffraction. The X-ray will hit the crystal face of sample at different angles. The results of the analysis have been compared with the standard phase to the chemical compounds of the samples.

Table 4.21: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratios of Cr.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Cr1000 ppm	47.5700	28.3600	10.4500	9.9800	50.300	29.000	4.100	13.600
Cr5000 ppm	54.5700	19.9700	10.4500	9.7800	37.500	41.800	2.500	15.400
Cr10000 ppm	57.0100	15.6600	11.9800	9.2100	22.100	54.800	2.400	17.100
Cr20000 ppm	62.1000	7.6200	12.2600	8.5100	17.300	59.100	1.600	19.100

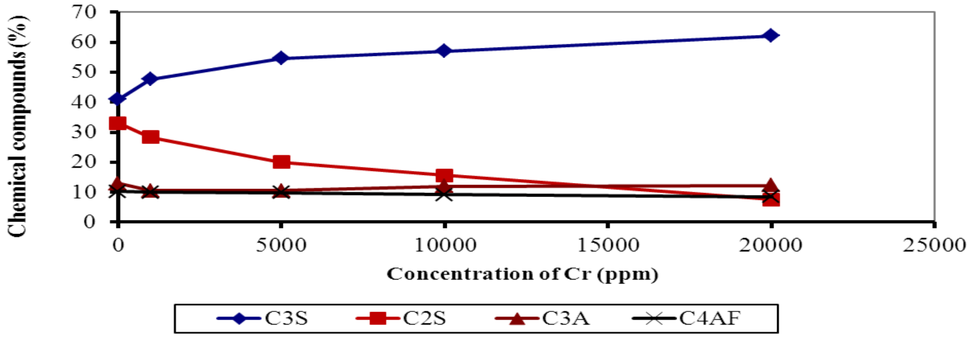
From Table 4.21 and Figure 4.19 (a) XRF, (b) XRD, as the result from XRF, belite was decreased, so amount of alite higher than belite because alite and belite were calculated by the formula as shown in equation 2.6 and 2.7 respectively.

$$C_3S = 4.07(CaO) - 7.60(SiO_2) - 6.72(Al_2O_3) - 1.43(Fe_2O_3) - 2.85(SO_3) \qquad (2.6)$$

$$C_2S = 2.87(SiO_2) - 0.75(3CaO \cdot SiO_2) \qquad (2.7)$$

As the results, the concentrations of chromium less than 0.5 wt.%, did not affect the phase of clinker because the chemical compounds calculated by equations of the amount of C_3S and C_2S from XRF in clinker such as CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3 were in the range of calibration curve and also the free lime content was less than 1.5% (Figure 4.13) which the clinker phases were formed completely. However, the concentrations of chromium were more than 0.5 wt.%, they would affect the calculation values of C_3S and C_2S when the free lime content was over than 1.5%. Moreover, the amounts of chemical compounds were detected outside the calibration curve (XRF) that the analysis result of C_3S was increased then the C_2S was decreased equal to 2.87(SiO_2) – 0.75(C_3S). Thus, the XRD has been used to analyze for the concentration of chemical compounds in clinker when the free lime content was more than 1.5%. Furthermore, the color of clinker that contains Cr was green.

(a) XRF



(b) XRD

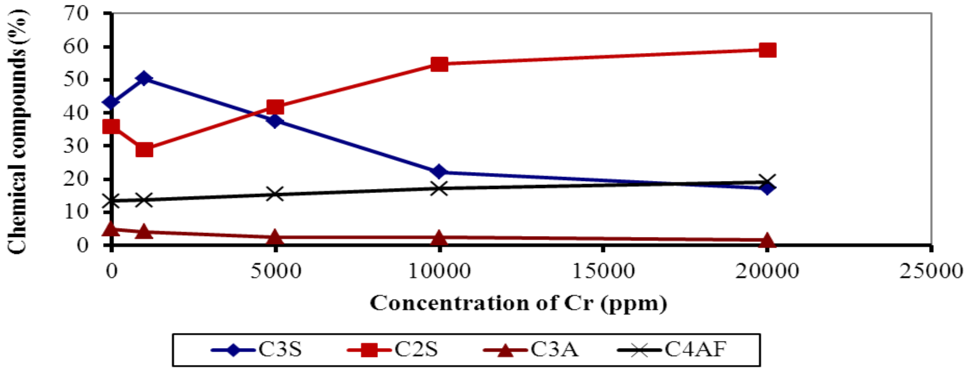


Figure 4.19: Concentrations of chemical compounds in clinker at different ratios of Cr (a) XRF and (b) XRD

The high chromium concentrations have affected to alite (C_3S) and belite (C_2S) formed because of increase concentration of Cr into the raw meal made decreased concentration of C_3S into the clinker phase as shown in Figure 4.19b. Between 0.5 to 2.0 wt.% of chromium, the content of alite was decreased and the content of belite was higher than alite by XRD because Chromium made the effect on alite phase and Chromium can prohibit the C_2S to change into C_3S as shown in equation 2.3 (Stephan et al., 1999a) as well as the free lime content was more than 1.5% which the clinker phases were formed incompletely.

$$CaO + 2CaO{\cdot}SiO_2 \longrightarrow 3CaO{\cdot}SiO_2 \qquad (2.3)$$

The comparison of the XRD patterns between control clinker and control which added Cr at 10000ppm (Figure 4.20) showed that the peak of Cr has appeared to form chemical compound. Some effects of the chromium on the chemical composition in clinker were described by previous researches. Kolovos et al., found that at 1 wt.% of CrO_3 added in raw meal was burned at 1,450°C, chromium has affected to inhibit alite formation reaction, the alite (C_3S) decomposed into belite (C_2S) and CaO in addition, occurring a new compound such as $Ca_4A_{l6}O_{12}Cr_4$ and $Ca_6A_{l4}Cr_2O_{15}$. Stephan et al., found at 2.5 wt.% of chromium, the content of belite (C_2S) was always higher than that of alite (C_3S). In addition, due to alite is formed by the reaction between belite and CaO. When chromium presented in the raw material, chromium would inhibit the reaction between belite and CaO to form alite ($CaO + 2CaO \cdot SiO_2 \rightarrow 3CaO \cdot SiO_2$). Malozhon et al (1971) also found the same results a concentration of 1.5 wt.% of Cr_2O_3 in the sample, had an effect to decrease a content of C_3S in clinker.

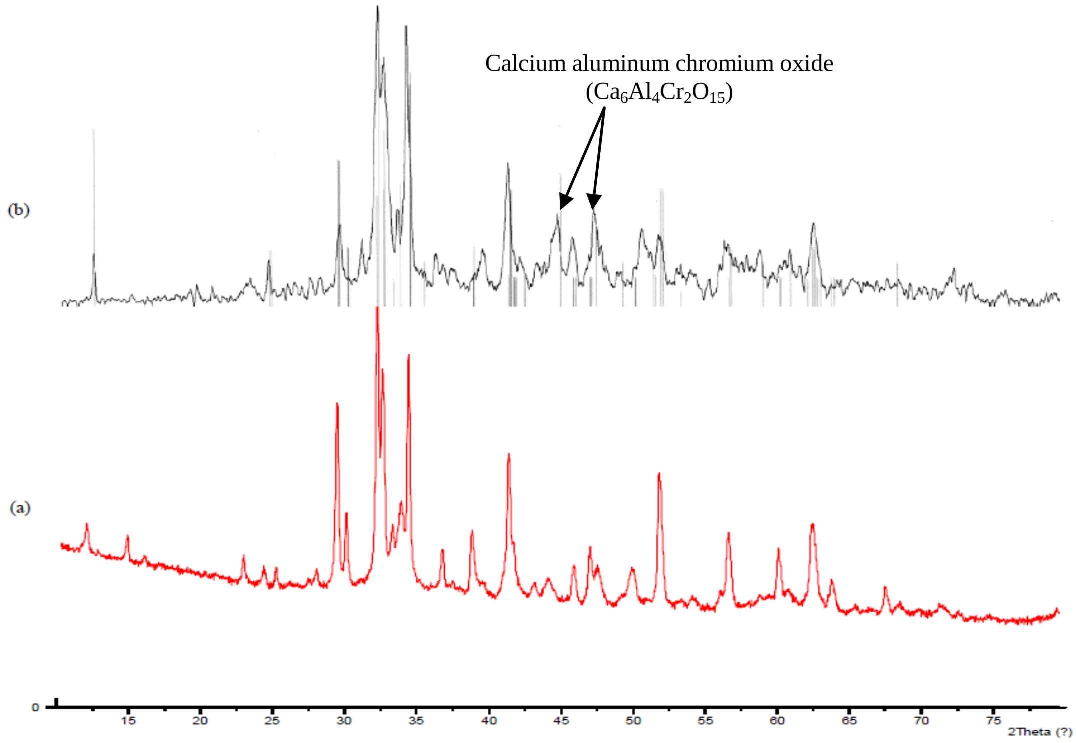


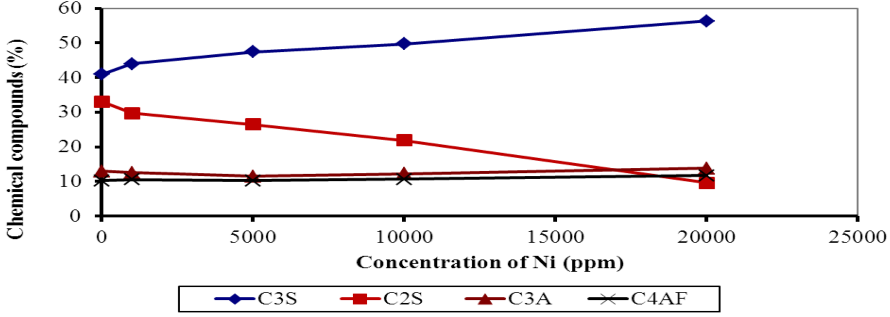
Figure 4.20: The XRD patterns of chemical compounds in clinker;
(a) Control and (b) Control + Cr

The comparison of the effect of Ni to chemical compositions of clinker were shown in Table 4.22 and Figure 4.21 (a) XRF and (b) XRD, as the result from XRF, belite was decreased, when the amount of alite increased because alite and belite were calculated by the formula as shown in equation 2.6 and 2.7 respectively. Thus, Ni had effect on the C_2S at 2.0%wt of Ni. Although the result from XRD showed that the concentrations of Ni between 0.1 up to 1.0 wt.% did not have an effect on the formation of C_3S, C_2S, C_3A, and C_4AF in the clinker phase even through rose up the concentration of Ni into raw meal for burning process as well as the free lime content was less than 1.5% which the clinker phases were formed completely. However, concentration of Ni at 2.0 %wt. has affected on the C_2S and C_3S which C_3S was gradually decreased when increasing concentration of Ni into the raw meal (Figure 4.21b). The comparison of the XRD patterns between control clinker and control which added Ni at 10000 ppm (Figure 4.22) showed that the peak of Ni has appeared to form chemical compound. Furthermore, at 2.0%wt. of Ni the color of clinker becomes dark brown.

Table 4.22: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratios of Ni.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Ni1000 ppm	43.9800	29.6800	12.5800	10.5300	45.300	32.600	4.800	15.600
Ni5000 ppm	47.4000	26.5000	11.4700	10.2600	44.300	34.000	4.600	14.300
Ni10000 ppm	49.6500	21.8300	12.1900	10.6400	47.100	27.500	5.300	17.100
Ni20000 ppm	56.2700	9.5900	13.7900	11.7300	38.700	32.100	6.900	16.900

(a) XRF



(b) XRD

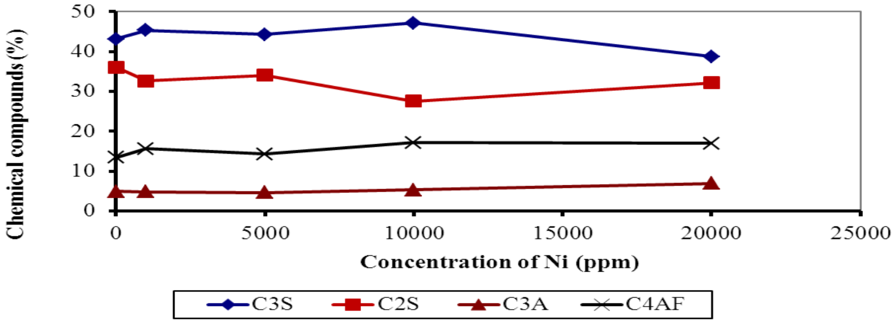


Figure 4.21: Concentrations of chemical compounds in clinker at different ratios of Ni; (a) XRF and (b) XRD

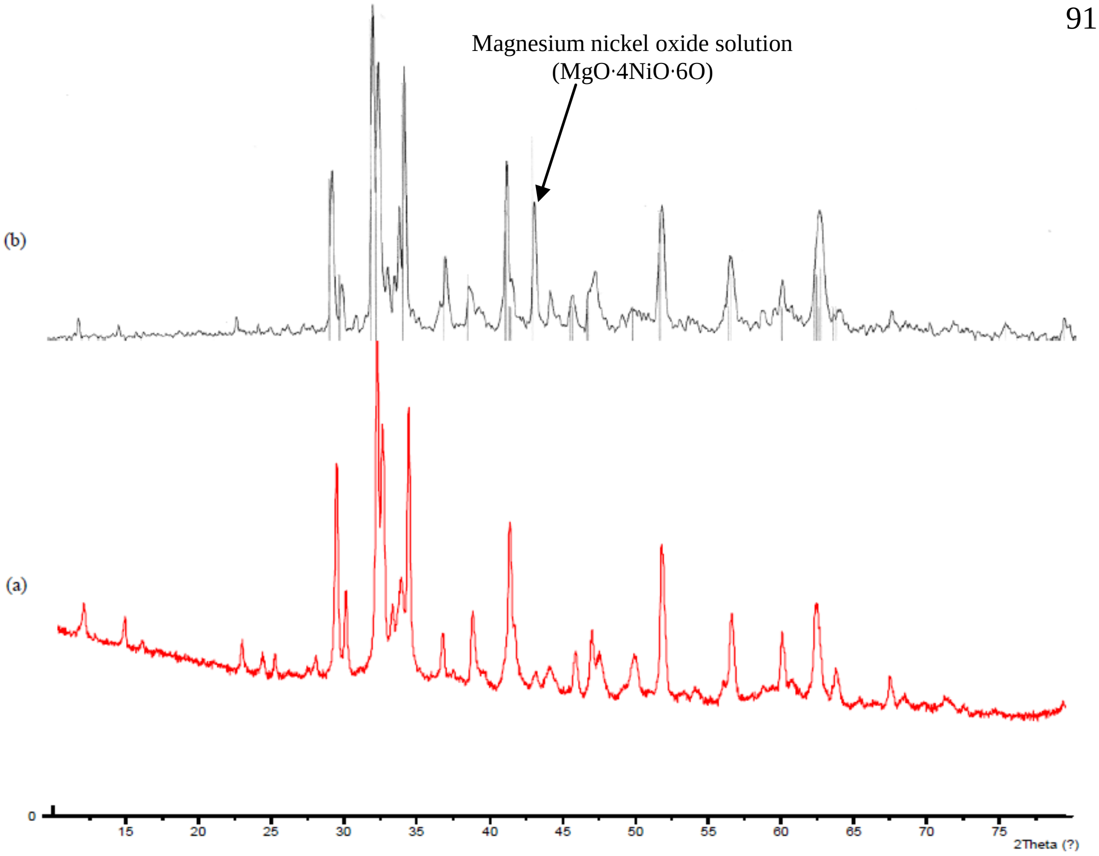


Figure 4.22: The XRD patterns of chemical compounds in clinker;
(a) Control and (b) Control + Ni

There are some studies that related to the effect of Ni on the chemical mineral phase of clinker. Stephan et al (1999a) reported that $MgNiO_2$ was found in the clinker containing with nickel and high concentrations of Mg and found a new phase in clinker doped with nickel that had a composition similar to $MgNiO_2$ and $MgNiO_2$ was a hydrated form which could not have reacted with water;therefore, these compounds could be the reason for the less leachability of nickel from cement. Thus, concentration of Mg in alite decreased due to occuring as $MgNiO_2$ and nickel was found in the aluminate and ferrite phase that the metals are concentrated in the ferrite phase because of the affinity of the transition metals for iron. Taweekitwanit (2004) found that the Ni was found in clinker after burning as well as Ni and Mg was reacted and formed a new phase which was $MgNiO_2$.

The comparison of the effect of Cu to chemical compositions of clinker was shown in Table 4.23 and Figure 4.23 (a) XRF and (b) XRD, As the result from XRF, belite (C_2S) was decreased, when the amount of alite (C_3S) increased and also the amount of alite higher than belite because alite and belite were calculated by the formula as shown in equation 2.6 and 2.7 respectively.

$$C_3S = 4.07(CaO)–7.60(SiO_2)–6.72(Al_2O_3)–1.43(Fe_2O_3)–2.85(SO_3) \qquad (2.6)$$

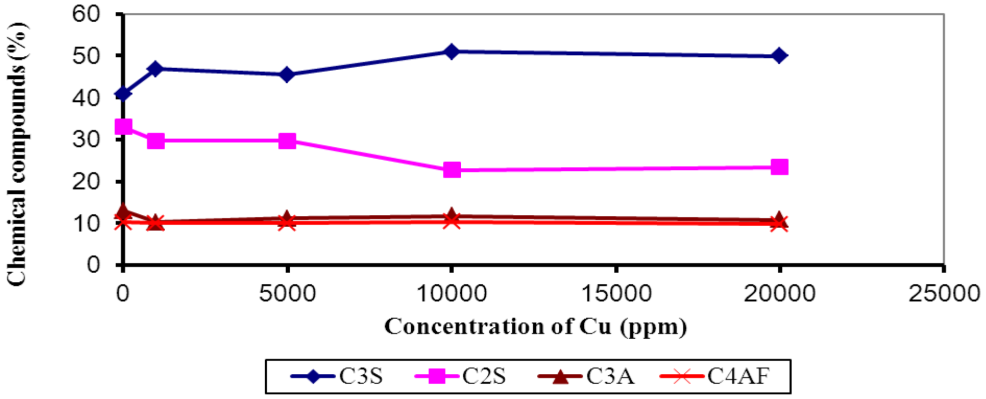
$$C_2S = 2.87(SiO_2) – 0.75(3CaO·SiO_2) \qquad (2.7)$$

As the results, the concentrations of Cu less than 0.5 wt.%, did not affect the phase of clinker due to the equations were calculated the amount of C_3S and C_2S by XRF, the chemical compounds in clinker such as CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3 were in the range of of calibration curve and also the free lime content was less than 1.5% (Figure 4.15) which the clinker phases were formed completely. However, the concentrations of Cu were more than 0.5 wt.%, have affected the calculation values of C_3S and C_2S when the free lime content was more than 1.5% as well as the amounts of chemical compounds were detected outside the calibration curve that the analysis result of C_3S was increased then the C_2S was decreased because of C_2S is equal to $2.87(SiO_2) – 0.75(C_3S)$. Thus, the XRD has been used to analyze for the concentration of chemical compounds in clinker when the free lime content was more than 1.5%. The high copper (Cu) concentrations have affected to alite (C_3S) and belite (C_2S) formed because of increasing concentration of Cu was over than 0.5%wt. into the control made decreased concentration of C_3S into the clinker phase as shown in Figure 4.23 (b) XRD. However, the concentration of Cu less than 0.5 wt.%, does not affect to the phase of clinker. Between 1.0 to 2.0 wt.% of Cu, the content of C_3S was decreased extremely and the contents of C_2S, C_4AF were higher than C_3S because Cu made the affect into alite phase and Cu can prohibit the C_2S to change into C_3S ($CaO + 2CaO·SiO_2 \rightarrow 3CaO·SiO_2$); Moreover, the color of clinker that contains 2.0%wt. of Cu was light brown. The comparison of the XRD patterns between control clinker and control which added Cu at 10000ppm (Figure 4.24) showed that the peak of Cu has appeared to form chemical compound. Ma et al (2006) found that at 0.1%wt. CuO is the content of C_3S reach the peak at 1300 °C and also CuO was increased in the range of 0.1% to 0.3%, gradually decreases the amount of C_3S formed. However, the contents of C_3S increases when the concentration of CuO was more than 0.3%. Kakali et al (1996) found that the addition of CuO affects the formation of silicates and alluminates. Especially, CuO promotes the formation of the alite crystals at lower temperature.

Table 4.23: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratios of Cu.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Cu1000 ppm	46.8400	29.6900	10.2700	10.0500	52.700	27.000	3.600	13.800
Cu5000 ppm	45.4900	29.7300	11.1600	10.0300	48.500	29.500	3.300	15.200
Cu10000 ppm	50.9200	22.6800	11.6900	10.3500	8.600	58.100	3.900	18.900
Cu20000 ppm	49.9200	23.3900	10.8400	9.7400	12.600	54.500	3.600	19.000

(a) XRF



(b) XRD

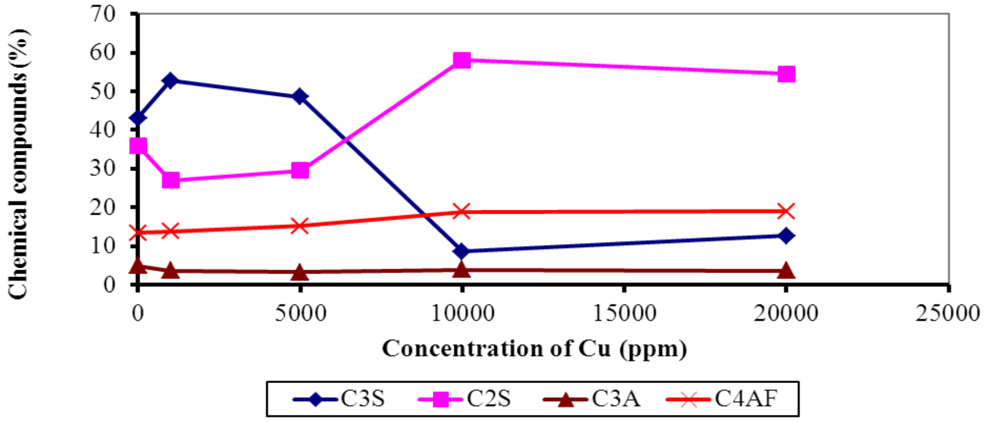


Figure 4.23: Concentrations of chemical compounds in clinker at different ratios of Cu; (a) XRF and (b) XRD

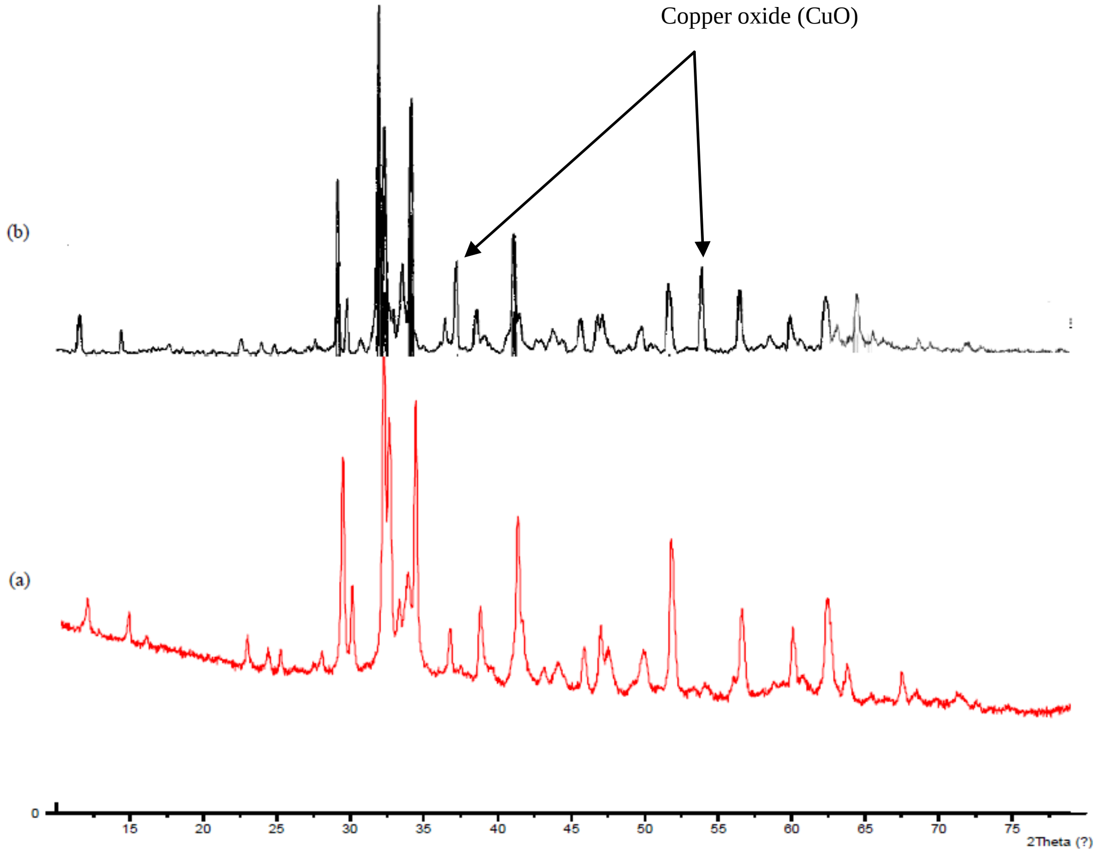


Figure 4.24: The XRD patterns of chemical compounds in clinker;

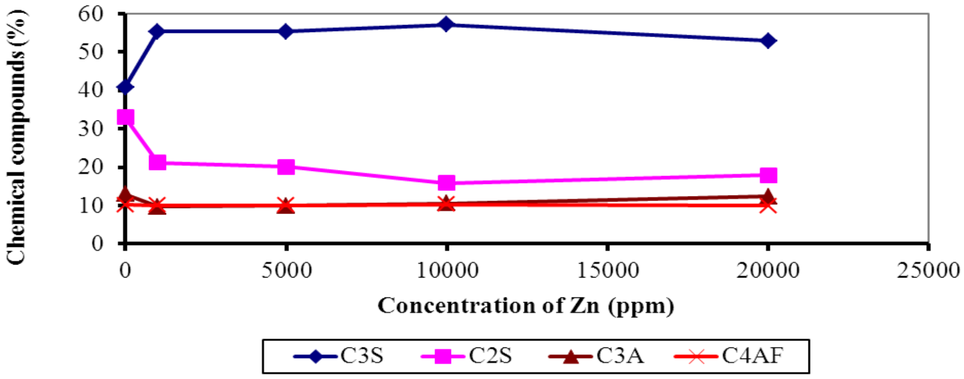
(a) Control and (b) Control + Cu

The comparison of the effect of Zn to chemical compositions of clinker were shown in Table 4.24 and Figure 4.25 (a) XRF and (b) XRD, as the result from XRF, the increasing of ZnO had affected on the content of C_3S increased, but C_2S was decreased because the contents of C_3S and C_2S were calculated by the formula as shown in equation 2.6 and 2.7 respectively. However, Zn did not effect on the C_3A and C_4AF formed. The result from XRD showed that the concentrations of Zn between 0.1 up to 2.0 wt.% did not have an effect on the formation of C_3S, C_2S, C_3A, and C_4AF in the clinker phase as well as the free lime content was less than 1.5% which the clinker phases were formed completely. The comparison of the XRD patterns between control clinker and control which added Zn at 10000 ppm (Figure 4.26) showed that the peak of Zn appeared to form chemical compound. Moreover, at 2.0% by wt. of Zn the color of clinker was brown to dark and the chemical mineral value in clinker accepted to the range of basic standard. From previous studies, Stephan et al. (1999) found that 2.5% of Zn small increased of C_3S and as corresponding decrease of C_2S. Andrade found 1% of ZnO in didn’t make the effect in chemical mineral into clinker. Furthermore, Knofel (1978) investigated that 4.0%wt. of Zn didn't make the effect to C_3S and C_2S, but increased concentration of C_4AF and reduction to C_3A.

Table 4.24: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratios of Zn.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Zn1000 ppm	55.3500	21.1800	9.6900	10.0600	53.000	28.000	3.300	13.600
Zn5000 ppm	55.3700	20.0400	9.8900	10.0400	47.900	32.700	2.800	14.400
Zn10000 ppm	57.1400	15.8800	10.6100	10.2700	48.300	27.200	2.900	17.000
Zn20000 ppm	52.9400	17.8800	12.4200	9.9200	43.000	34.000	3.900	16.300

(a) XRF



(b) XRD

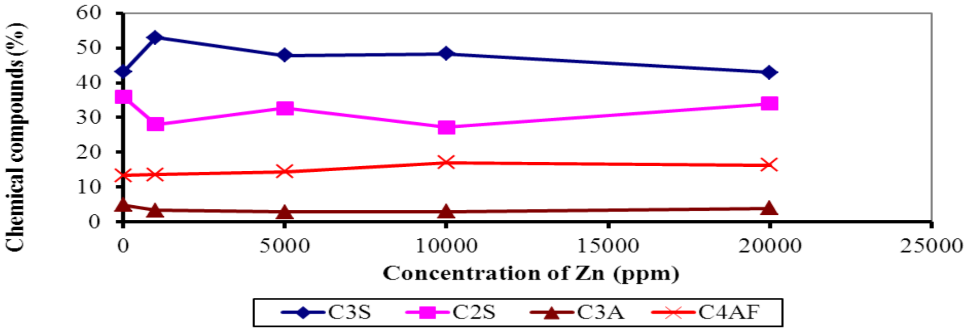


Figure 4.25: Concentrations of chemical compounds in clinker at different ratios of Zn; (a) XRF and (b) XRD

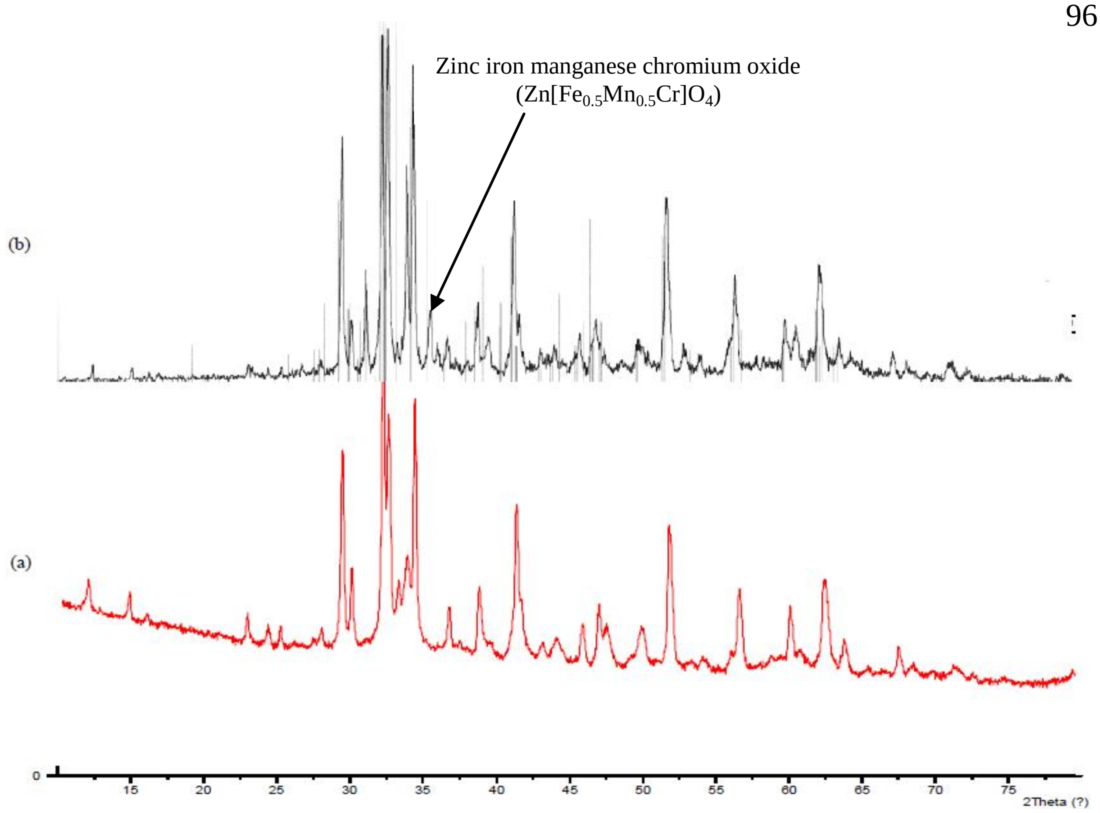


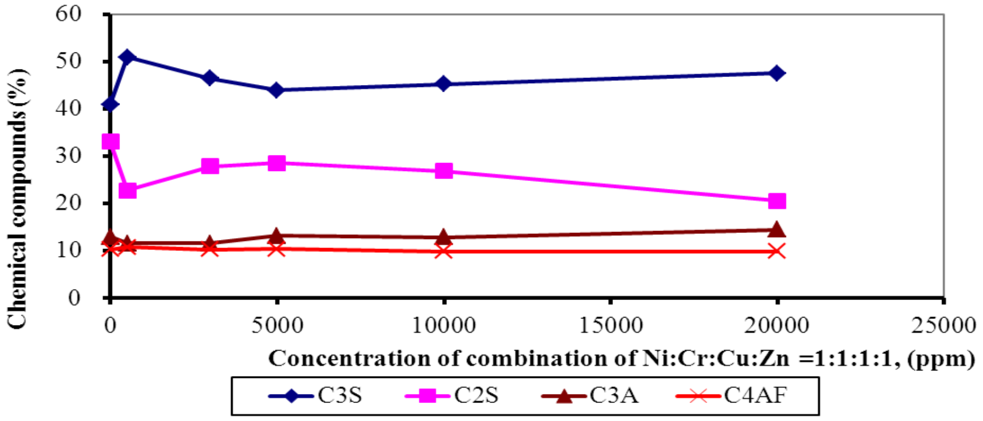
Figure 4.26: The XRD patterns of chemical compounds in clinker;
(a) Control and (b) Control + Zn

Table 4.25 and Figure 4.27 (a) XRF and (b) XRD show the comparison of chemical oxide and chemical compounds between in the clinker control and in clinker samples with different amounts of combination of heavy metal of Ni:Cr:Cu:Zn =1:1:1:1, as the result of XRF with different amounts of heavy metals, high concentration between 1.0 to 2.0 wt.% of heavy metals in the clinker was slightly decreased concentration of C_2S and C_4AF, but corresponding increased of C_3S and C_3A. The results was corresponding with addition of each pure heavy metal between 0.1 to 0.5 wt.% such as Cr, Ni, Cu and Zn because the contents of C_3S and C_2S were calculated by the formula as shown in equation 2.6 and 2.7 respectively. As the result of XRD with different amounts of heavy metals, high concentration between 1.0 to 2.0 wt.% of heavy metals in the clinker was gradually increased concentration of C_2S and C_4AF but reduced concentration of C_3S. Thus, at 2.0wt.% of heavy metals showed the amount of C_2S higher than C_3S. The results was corresponding with added pure of each heavy metal between 0.1 to 0.5 wt.% such as Cr and Cu which decreased of C_3S but increased of C_2S. Furthermore, the color of clinker that contains 0.5 wt.% Cr was green.

Table 4.25: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratio of combination of Ni:Cr:Cu:Zn =1:1:1:1.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Ni:Cr:Cu:Zn 500 ppm	50.8800	22.7500	11.5200	10.7300	45.900	30.900	5.000	14.800
Ni:Cr:Cu:Zn 3000 ppm	46.3500	27.8300	11.5000	10.2500	46.500	32.600	3.600	14.500
Ni:Cr:Cu:Zn 5000 ppm	43.9300	28.5100	13.1100	10.3800	41.800	35.700	4.700	15.300
Ni:Cr:Cu:Zn 10000 ppm	45.2400	26.8400	12.8700	9.8700	37.600	39.900	3.800	15.600
Ni:Cr:Cu:Zn 20000 ppm	47.5300	20.5700	14.3900	9.8700	29.400	46.800	2.700	17.300

(a) XRF



(b) XRD

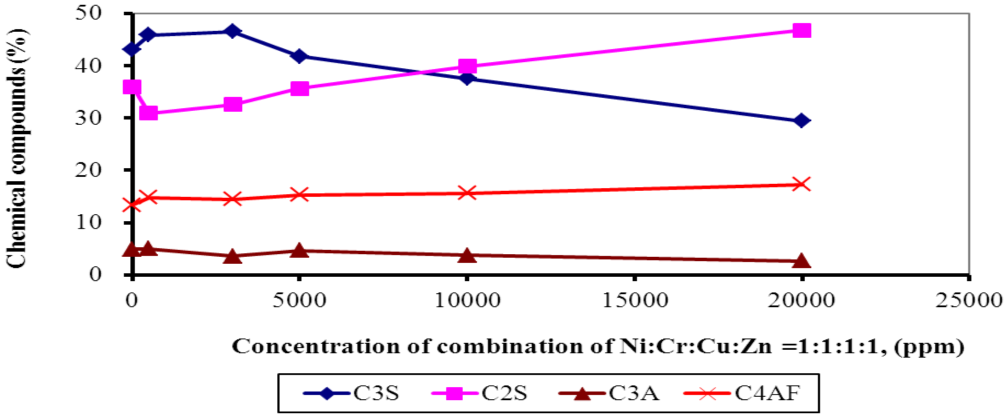
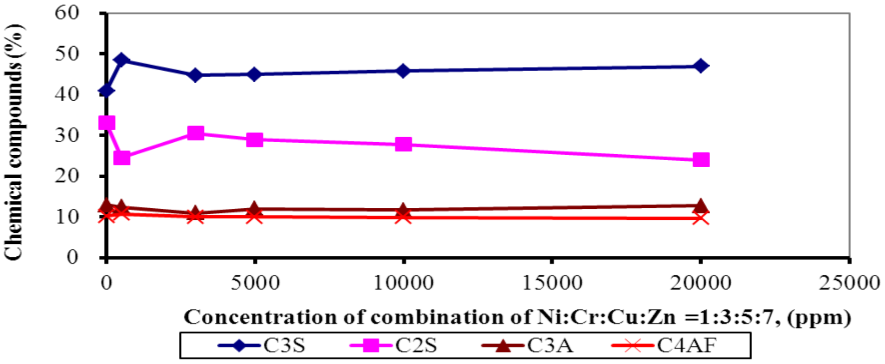


Figure 4.27: Concentrations of chemical compounds in clinker at different ratios of combination of Ni:Cr:Cu:Zn =1:1:1:1

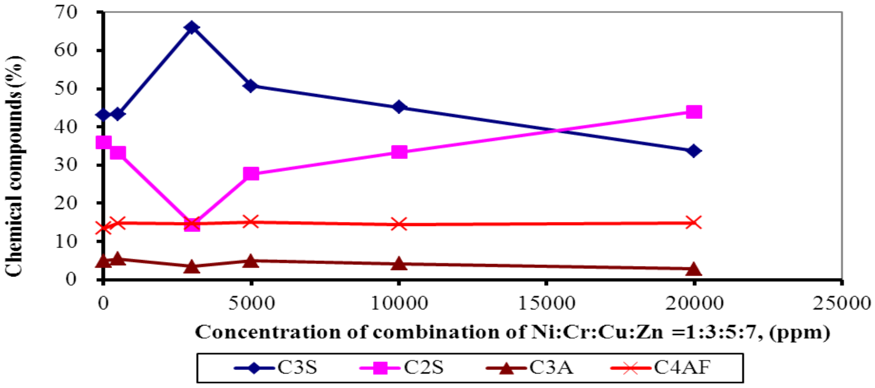
Same as the result of combination of heavy metal of Ni:Cr:Cu:Zn =1:3:5:7 (Table 26 and Figure 28 (a) XRF and (b) XRD), showed that the result of XRF with different amounts of heavy metals, high concentration between 1.0 to 2.0 wt.% of heavy metals in the clinker was slightly decreased concentration of C_2S and C_4AF, but corresponding slightly increased of C_3S. The results was corresponding with added pure of each heavy metal between 0.1 to 0.8 wt.% such as Cr, Ni, Cu and Zn because the contents of C_3S and C_2S were calculated by the formula as shown in equation 2.6 and 2.7 respectively. As the result of XRD with different amounts of heavy metals, high concentration at 2.0 wt.% of heavy metals in the clinker was gradually increased concentration of C_2S and C_4AF but reduced concentration of C_3S. Thus, at 2.0wt.% of heavy metals showed the amount of C_2S higher than C_3S. The results was corresponding with added pure of each heavy metal between 0.3 to 0.6 wt.% of Cr and Cu respectively which decreased of C_3S but increased of C_2S. Furthermore, the color of clinker that contains 0.3 wt.% Cr was light green.

Table 4.26: Comparison of chemical oxides and chemical compounds between in the clinker control and in clinker samples with different ratio of combination of Ni:Cr:Cu:Zn =1:3:5:7.

Clinker samples	Chemical Analysis (XRF)				Chemical Analysis (XRD)			
	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker from manufacturing	54.3600	23.0200	7.8500	11.0100	58.400	23.500	2.200	14.600
Control	40.8800	33.0400	12.9500	10.2200	43.100	36.000	4.900	13.400
Ni:Cr:Cu:Zn 500 ppm	48.4100	24.4800	12.3700	10.7100	43.300	33.200	5.400	14.800
Ni:Cr:Cu:Zn 3000 ppm	44.6900	30.4800	10.9800	9.9800	66.000	14.400	3.500	14.700
Ni:Cr:Cu:Zn 5000 ppm	44.9300	28.8800	12.0100	10.0200	50.700	27.700	4.900	15.100
Ni:Cr:Cu:Zn 10000 ppm	45.7200	27.7600	11.6600	9.8600	45.100	33.400	4.200	14.500
Ni:Cr:Cu:Zn 20000 ppm	46.9000	24.0000	12.7300	9.7000	33.700	44.000	2.800	14.900



(a) XRF



(b) XRD

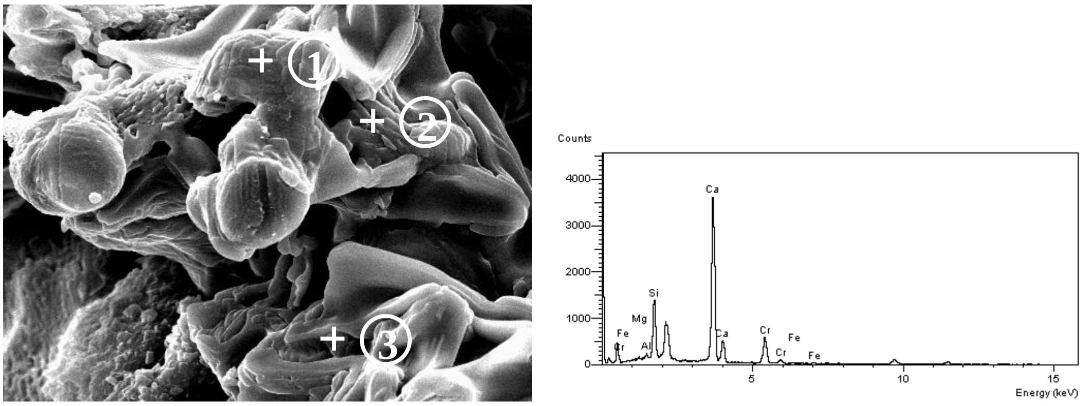
Figure 4.28: Concentrations of chemical compounds in clinker at different ratios of combination of Ni:Cr:Cu:Zn =1:3:5:7

These results are consistent with the study conducted by Shih, et al. (2005) found that when the concentration of Cr has increased over than 2.5%, the C_3S was decomposed into C_2S and low volatile heavy metals such as Ni, Cr, and Cu in the sludge were trapped in the clinker. Stephan, et al. (1999b) showed that 2.5% of Cr inhibited the C_2S reacted with CaO to set C_3S form, caused of found C_3S only 21.9%. However, 2.5wt.% of Zn small increased of C_3S and as corresponding decrease of C_2S and high Cr increased concentration of C_2S into clinker. Similarly to the studied of addition of Cr into the kiln feed sample caused of inhibit C_2S to set C_3S whereas Ni didn’t made the effect to chemical mineral in the clinker (Barros et al., 2004). The concentration of C_3S were reduced when added concentration of Cr around 1.5% wt. (Malozhon et al., 1971). Older, et al. (1980) found increased concentration of C_3S came from substitution of Zn for Ca. However, 1.0wt.% of ZnO in didn’t make the effect in chemical mineral into clinker as previously observed by Andrade, et al. (2003). Moreover, Ma, et al. (2006) found that when CuO was increased in the range of 0.1% to 0.3%, gradually decreases the amount of C_3S formed.

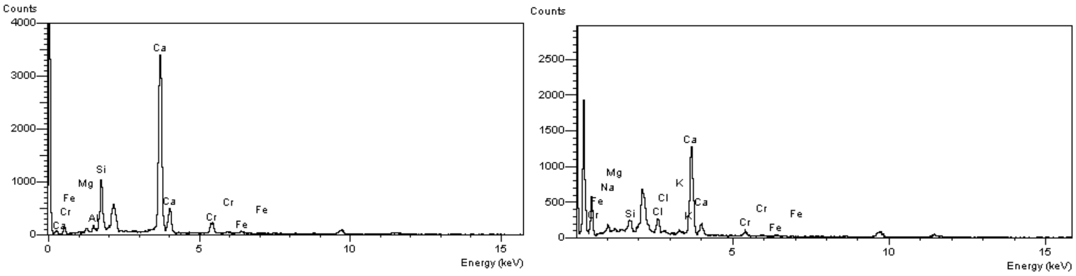
4.4 The phase of clinker at different amounts of heavy metals

Method of SEM-EDX was used to find the major elements in surface of the clinker and analysis of the characteristics of each concentration of heavy metals in 4 types. The concentrations with different ratios of heavy metals were analyzed by using SEM analysis as shown in Appendix E (Figure E.1 – E.28 and Table E.9-E.36); the samples were stuck by carbon tape and the spectrum from instrument was shot into three random positions of the samples into clinker phase such as the spectrums no. 1, 2 and 3 were shot into C_3S, C_3A & C_4AF and C_2S, respectively. In the clinker from manufacturing and control clinker that contained heavy metals in low concentration which they cannot be detected as shown in, Figure E.1 and E.2, the major phase of clinker showed that $C_3S(3CaO{\cdot}SiO_2)$, $C_2S(2CaO{\cdot}SiO_2)$, $C_3A(3CaO{\cdot}Al_2O_3)$ and $C_4AF(4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3)$. The SEM was zoomed 2000 times at the spectrum size of 20kv which it can detect the elements of clinker phase such as C (as $CaCO_3$), Si (as SiO_2), Ca (as $CaSiO_3$), Al, Fe, Mg, Ti, etc. Whereas the structure of molecules were K-line as shown in figure 2.6 in chapter II.

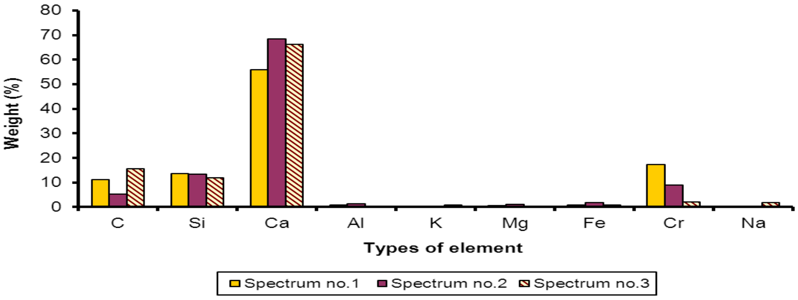
The clinker phase that contained chromium at different ratios was shown in Figure 4.29 and the elements was shown in Table 4.27. The SEM patterns of clinker which added Cr at 20000ppm showed that the peaks of Cr has appeared, so Cr was trapped by C_3S, C_4AF and C_2S. At 2.0 wt.% of Cr showed that C_3S was contained Cr equal to 17.25%, C_2S was contained Cr equal to 2.20%. Whereas, C_4AF was contained Cr equal to 8.83%. The result showed that the clinker samples which contained 0.1-2.0wt.% of Cr which have affected to the clinker phase as well as shape of C_3S and C_2S. Moreover, Cr reacted with Al and Fe in the clinker phase, and got new solution called calcium aluminate, calcium chloroaluminate, gehlenite calcium chromate and two types of ferrites (Murat and Sorrentino, 1996). Cr was concentrated in C_3S and C_2S and makes the size of them larger than usual (> 100 and 80-90µm, respectively). Incorporation of Cr not only in C_3S and C_2S, but also Cr reacted with K and got K_2CrO_4 and $K_2Cr_2O_7$. Therefore, the high chromium concentrations have affected to alite and belite formed (Opoczky and Gavel, 2004; Stephan et al., 1999b).



(a) Clinker phase 20kv x2000 (b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF) (d) Spectrum no.3 (C_2S)



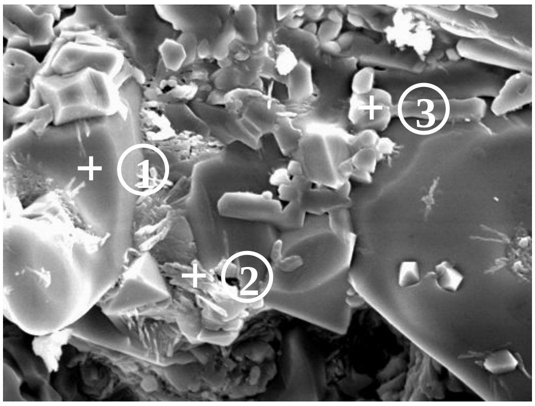
(e) The quantitative results of elements

Figure 4.29: Analysis of clinker phase with added Cr 20000 ppm: (a) clinker phase, (b) spectrum no.1 1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S), (e) the quantitative results of elements

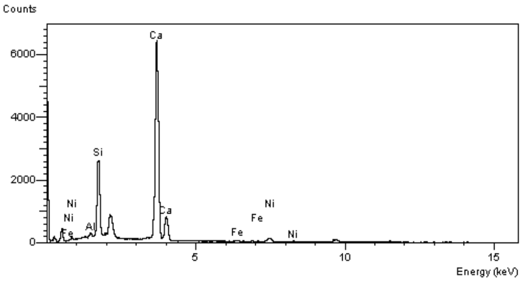
Table 4.27: The quantitative result of elements in the clinker phase with added Cr 20000ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	11.08	5.17	15.67
Si	13.54	13.36	11.98
Ca	55.9	68.45	66.19
Al	0.76	1.3	0
K	0	0	0.75
Mg	0.55	1.09	0.52
Fe	0.92	1.80	0.89
Cr	17.25	8.83	2.20
Na	0	0	1.80
Total	100	100	100

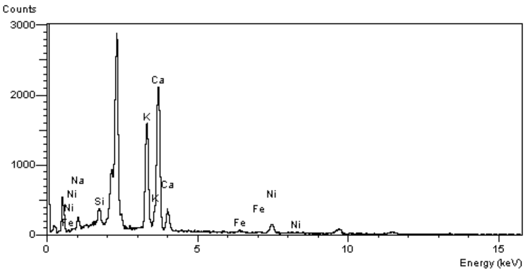
The clinker phase that contained nickel at different ratios was shown in Figure 4.30 and the elements was shown in Table 4.28. The SEM patterns of clinker which added Ni at 20000ppm showed that the peaks of Ni has appearred, so Ni was trapped by C_3S, C_4AF and C_2S. The addition of 2.0 wt.% Ni showed that C_3S was contained Ni equal to 4.45%, C_2S was contained Ni equal to 28.05%. Whereas, C_4AF was contained Ni equal to 8.85%. The result showed that the clinker samples which contained 0.1 -2.0%wt. of Ni which did not have an effect to the clinker phase as well as shape of C_3S and C_2S. Moreover, Ni was trapped in C_2S more than in C_4AF and C_3S respectively and also found that Mg influenced to Ni in C_2S. Same as the results of previous studies, Opoczky and Gavel (2004) found Ni incorporated into C_3S and C_2S and take up the place of the Ca^{2+} ion. Due to the size of Ni^{2+}ion smaller than Ca^{2+} ion, it does not cause of deformation of C_3S and C_2S. Stephan et.al (1999) found the Ni was reacted with Mg in burning process and got $MgNiO_2$ solution in clinker phase. Initial compound (NiO) was found in clinker after burning. Nickel and Mg was reacted and formed a new phase which was $MgNiO_2$ (Taweekitwanit, 2004).



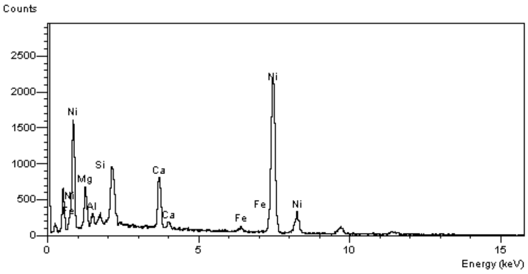
(a) Clinker phase 20kv x2000



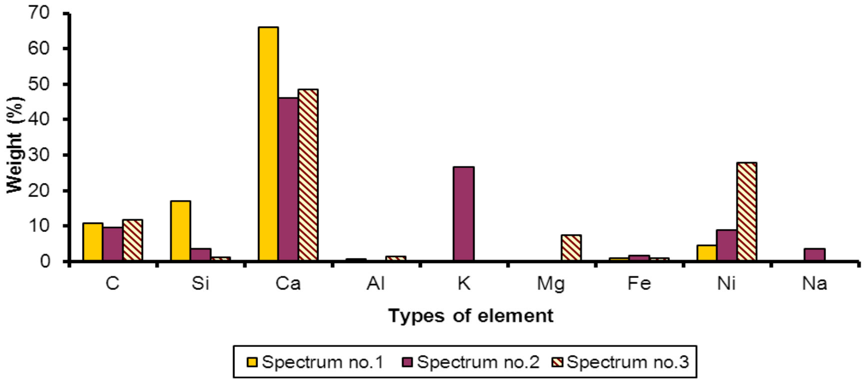
(b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF)



(d) Spectrum no.3 (C_2S)



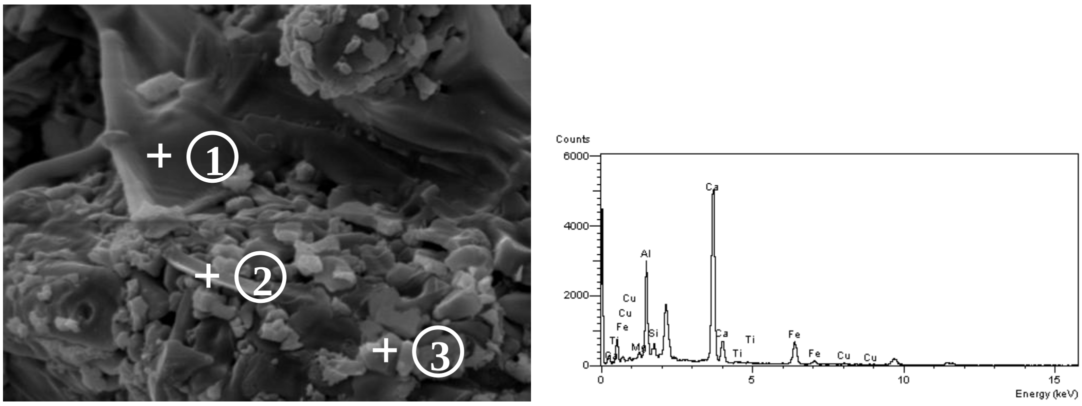
(e) The quantitative results of elements

Figure 4.30: Analysis of clinker phase with added Ni 20000 ppm: (a) clinker phase, (b) spectrum no.1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S), (e) the quantitative results of elements

Table 4.28: The quantitative result of elements in the clinker phase with added Ni 20000 ppm.

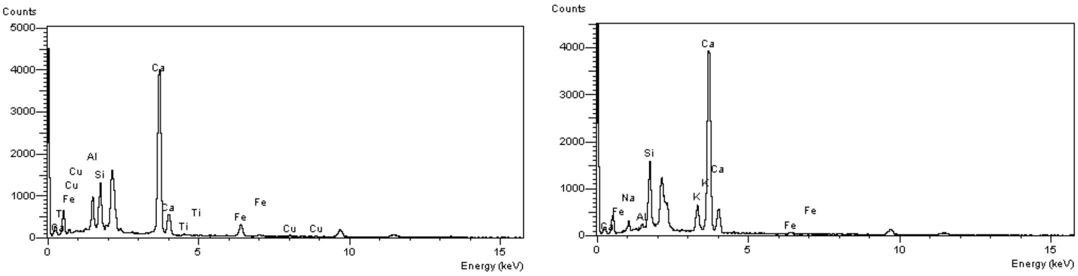
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.8	9.51	11.9
Si	16.99	3.63	1.39
Ca	66.15	46.04	48.63
Al	0.66	0	1.46
K	0	26.61	0
Mg	0	0	7.49
Fe	0.95	1.67	1.08
Ni	4.45	8.85	28.05
Na	0	3.69	0
Total	100	100	100

The clinker phase that contained copper at different ratios was shown in Figure 4.31 and the elements was shown in Table 4.29. The SEM patterns of clinker which added Cu at 20000ppm showed that the peaks of Cu has appearred, so Cu was trapped by C_3S and C_4AF as well as also found Cu in C_2S at 1.0wt% of Cu (Figure E.13 in Appendix E). The addition of 2.0 wt.% Cu showed that C_3S was contained Cu equal to 1.52%, C_4AF was contained Cu equal to 1.46%, but Cu was not detected in C_2S. The result showed that the clinker samples which contained 0.1 -2.0%wt. of Cu which have affected to the clinker phase as well as shape of C_3S and C_2S. Moreover, Cu was trapped in C_3S more than in C_4AF and also found Fe and Al influenced to Cu in C_3S as well as C_4AF. Same as the results of previous studies, Kolovos et al., (2005) found that Cu which is cation ion, could have positive or marginal effect on the reactivity of CaO–SiO2–Al2O3–Fe2O3 mixtures. Ract et al., (2003) found that the additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.%Cu to clinker raw-material do not affect the clinkering reactions and over 99 wt.% of Cu were incorporated into the clinker during the burning process.



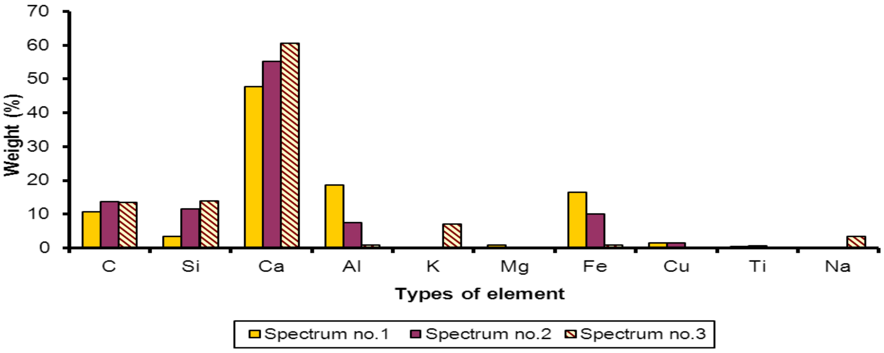
(a) Clinker phase 20kv x2000

(b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF)

(d) Spectrum no.3 (C_2S)



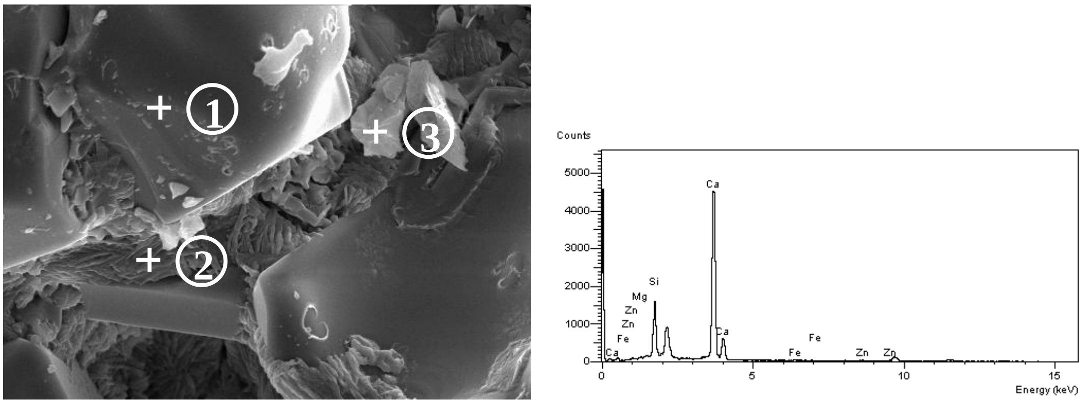
(e) The quantitative results of elements

Figure 4.31: Analysis of clinker phase with added Cu 20000 ppm: (a) clinker phase, (b) spectrum no.1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S) (e) the quantitative results of elements

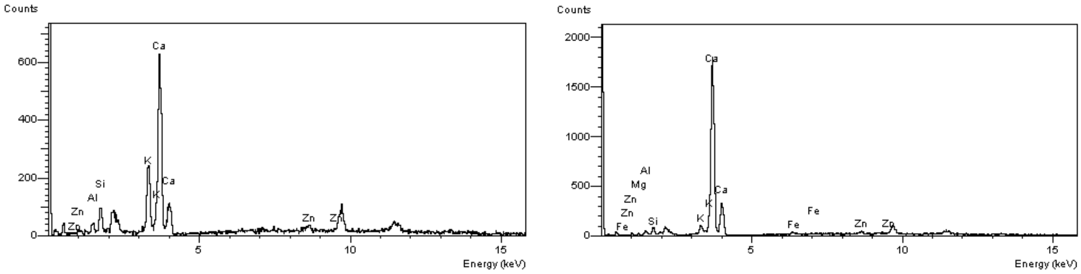
Table 4.29: The quantitative result of elements in the clinker phase with added Cu 20000 ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.77	13.73	13.38
Si	3.51	11.57	13.96
Ca	47.78	55.16	60.56
Al	18.62	7.55	0.75
K	0	0	7.06
Mg	0.91	0	0
Fe	16.39	9.99	0.95
Cu	1.52	1.46	0
Ti	0.5	0.54	0
Na	0	0	3.34
Total	100	100	100

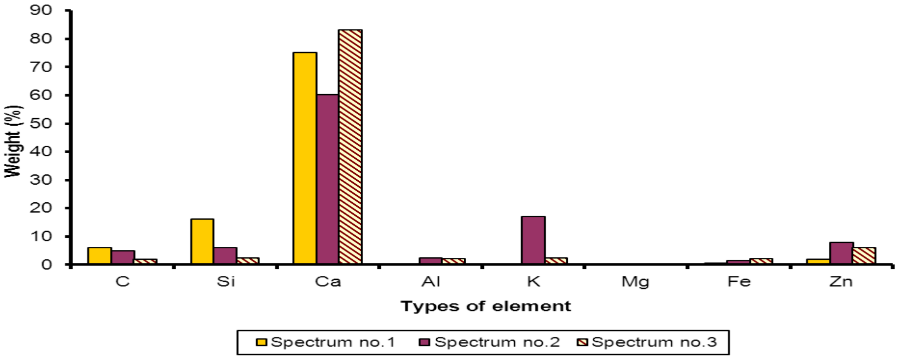
The clinker phase that contained zinc at different ratios was shown in Figure 4.32 and the elements was shown in Table 4.30. The SEM patterns of clinker which added Zn at 20000 ppm showed that the peaks of Zn has appearred, so Zn was trapped by C_3S, C_2S and C_4AF. The addition of 2.0 wt.% Zn showed that C_3S was contained Zn equal to 1.84%, C_4AF was contained Zn equal to 7.78%; whereas, C_2S was contained Zn equal to 5.94%. The result showed that the clinker samples which contained 0.1 -2.0wt.% of Zn did not have an effect to the clinker phase, but Zn created large size of C_3S. Moreover, Zn was trapped in C_4AF more than in C_2S and in C_3S respectively and also found Fe and Al influenced to Zn in C_2S as well as C_4AF. Same as the results of previous studies, Andrade et al. (2002) found Zn more easily incorporated in C_3S. Murat and Sorrentino (1996) found Zn reacted with Fe in clinker and created large size in C_3S. Older et al. (1980) gave information that increased C_3S was due to substitution of Zn for Ca. 53% of zinc was fixed in Portland cement clinker, and ZnO addition increased the alite size crystals (Murat et al., 1996).



(a) Clinker phase 20kv x2000 (b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF) (d) Spectrum no.3 (C_2S)



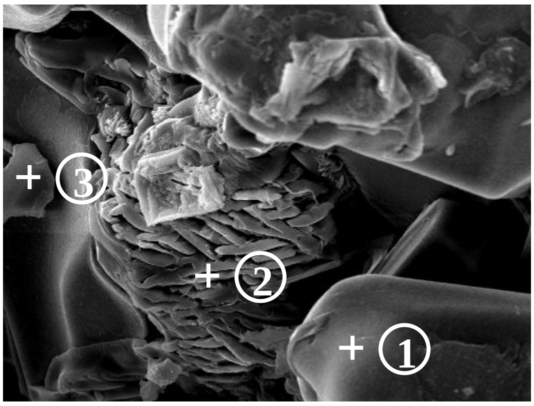
(e) The quantitative results of elements

Figure 4.32: Analysis of clinker phase with added Zn 20000 ppm: (a) clinker phase, (b) spectrum no.1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S) (e) the quantitative results of elements

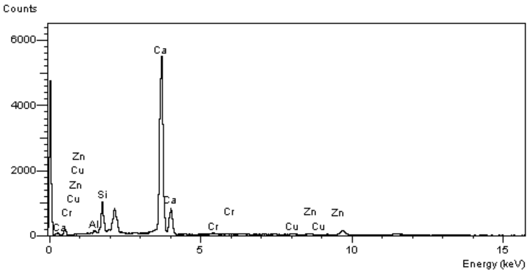
Table 4.30: The quantitative result of elements in the clinker phase with added Zn 20000 ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	5.97	4.90	1.83
Si	16.08	6.06	2.32
Ca	75.06	60.33	83.02
Al	0	2.29	2.05
K	0	17.17	2.39
Mg	0.41	0	0.33
Fe	0.64	1.47	2.12
Zn	1.84	7.78	5.94
Total	100	100	100

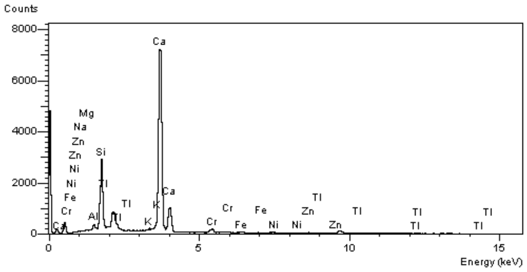
The clinker phase that contained the combination of heavy metals at different ratios of Ni:Cr:Cu:Zn as shown in Figure 4.33 and the elements has shown in Table 4.31. The SEM patterns of clinker which added heavy metals at 20000 ppm showed that the peaks of Cr, Cu, Ni and Zn has appearred, so all heavy metals were trapped by C_3S, C_2S and C_4AF. At 2.0 wt.% of heavy metals ratio 1:1:1:1 showed that C_3S were contained Cr, Cu and Zn equal to 1.02%, 2.15% and 1.33% respectively. C_2S were contained Cr, Cu and Ni equal to 1.13%, 0.78% and 1.96% respectively. Whereas, C_4AF were contained Cr, Zn and Ni equal to 2.71%, 0.74% and 0.91% respectively. The result showed that the clinker samples which contained 0.1 - 2.0wt.% of combination of heavy metals which did not have an effect to the clinker phase, but Zn created large size of C_3S. Moreover, Cr was trapped in C_4AF more than in C_2S and in C_3S respectively. Cu was trapped in C_3S more than in C_2S, but Ni was trapped in C_2S more than C_4AF. Finally, Zn was trapped in C_3S more than in C_3S, and also found Fe and Al influenced to Zn, Cr and Ni in C_4AF.



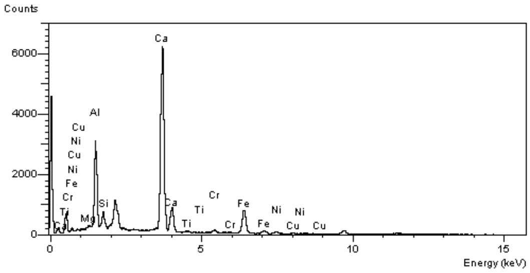
(a) Clinker phase 20kv x2000



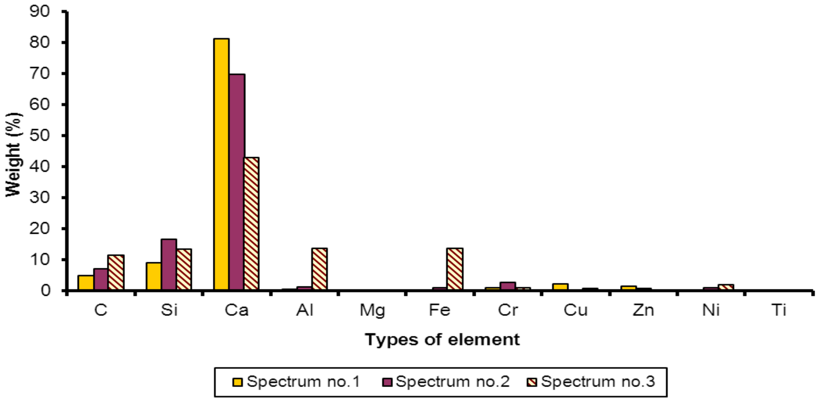
(b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF)



(d) Spectrum no.3 (C_2S)



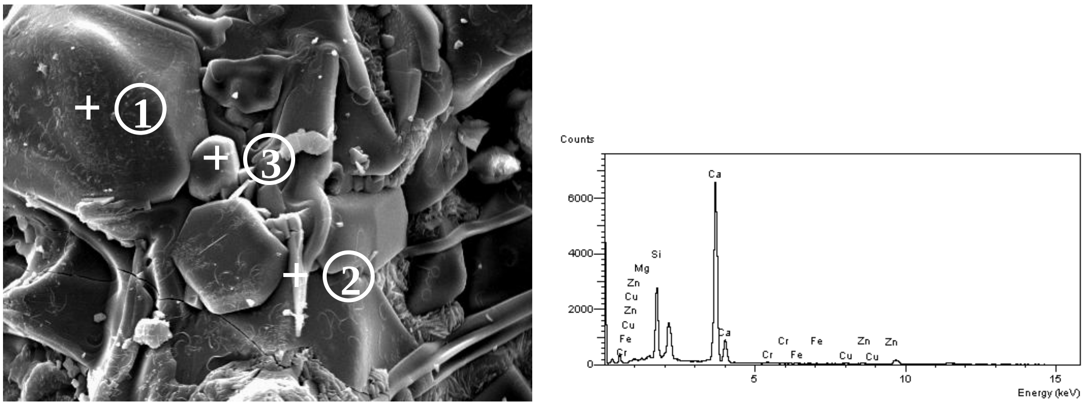
(e) The quantitative results of elements

Figure 4.33: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 20000ppm (a) clinker phase, (b) spectrum no.1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S) (e) the quantitative results of elements

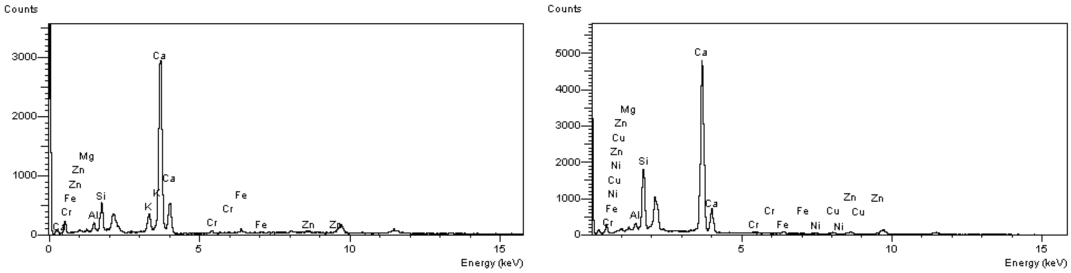
Table 4.31: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 20000ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	4.75	7.12	11.54
Si	9.08	16.55	13.39
Ca	81.12	69.68	42.86
Al	0.55	1.13	13.71
Mg	0	0.3	0.36
Fe	0	0.86	13.73
Cr	1.02	2.71	1.13
Cu	2.15	0	0.78
Zn	1.33	0.74	0
Ni	0	0.91	1.96
Ti	0	0	0.54
Total	100	100	100

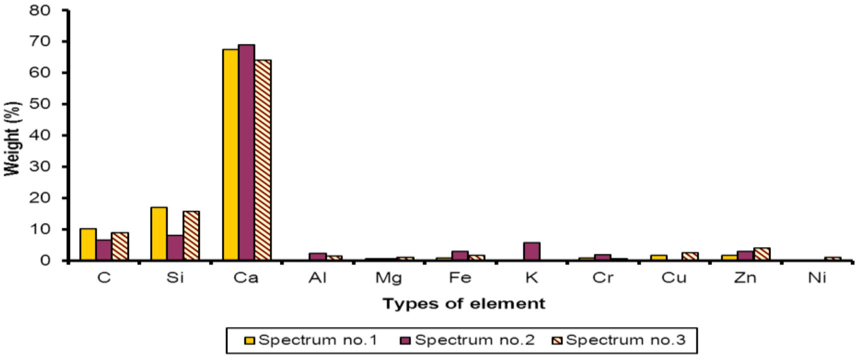
The clinker phase that contained the combination of heavy metals at different ratios of Ni:Cr:Cu:Zn 1:3:5:7 as shown in Figure 4.34 and the elements has shown in Table 4.32. The SEM patterns of clinker which added heavy metals at 20000ppm showed that the peaks of Cr, Cu, Ni and Zn has appearred, so all heavy metals were trapped by C_3S, C_2S and C_4AF. At 2.0 wt.% of heavy metals ratio 1:3:5:7 showed that C_3S were contained Cr, Cu and Zn equal to 0.78%, 1.62% and 1.67% respectively. C_2S were contained Cr, Cu, Zn and Ni equal to 0.53%, 2.46%, 3.83% and 0.96% respectively. Whereas, C_4AF contained Cr and Zn equal to 1.97% and 2.87% respectively. The result showed that the clinker samples which contained 0.1 - 2.0wt.% of combination of heavy metals which did not have an effect to the clinker phase, but Zn created large size of C_3S. Moreover, Cr was trapped in C_4AF more than in C_3S and in C_2S respectively. Cu was trapped in C_2S more than in C_3S, but Ni was trapped in C_2S. Finally, Zn was trapped in C_2S more than in C4AF and in C_3S respectively, and also found Fe and Al influenced to Cu, Zn, Cr and Ni in C_4AF and C_2S.



(a) Clinker phase 20kv x2000 (b) Spectrum no.1 (C_3S)



(c) Spectrum no.2 (C_4AF) (d) Spectrum no.3 (C_2S)



(e) The quantitative results of elements

Figure 4.34: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 20000ppm (a) clinker phase, (b) spectrum no.1 (C_3S), (c) spectrum no.2 (C_4AF), (d) spectrum no.3 (C_2S) (e) the quantitative results of elements

Table 4.32: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 20000 ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.17	6.48	8.73
Si	17.03	8.13	15.65
Ca	67.47	69.06	64.07
Al	0	2.23	1.29
Mg	0.49	0.62	0.99
Fe	0.77	2.89	1.49
K	0	5.76	0
Cr	0.78	1.96	0.53
Cu	1.62	0	2.46
Zn	1.67	2.87	3.83
Ni	0	0	0.96
Total	100	100	100

Previous researchers have some project that related to the effect of heavy metal into chemical mineral phase of clinker. The additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.%Cu and 1.2 wt.% Ni to clinker raw-material do not affect the clinkering reactions and all Ni and over 99 wt.% of Cu were incorporated into the clinker during the burning process (Ract et al., 2003). Shih et al. (2005) found that when the concentration of Cr has increased over than 2.5%, the C_3S was decomposed into C_2S and low volatile heavy metals such as Ni, Cr, and Cu in the sludge were almost totally trapped in the clinker. Murat, et al. (1996) found that a large amount of chromium (84%) was trapped and 53% of zinc was fixed in Portland cement clinker. Also, ZnO addition increased the alite size crystals. Older, et al. (1980) found increased concentration of C_3S came from substitution of Zn for Ca. Cr reacted with Al and Fe in the clinker phase, and got new solution called calcium aluminate, calcium chloroaluminate, gehlenite calcium chromate and two types of ferrites (Murat and Sorrentino, 1996). Cr was concentrated in C_3S and C_2S and makes the size of them larger than usual (> 100 and 80-90µm, respectively). Incorporation of Cr in C_3S and C_2S also caused of made green color in clinker (Opoczky and Gavel, 2004). Moreover, Cr reacted with K and got K_2CrO_4 and $K_2Cr_2O_7$. Therefore, the high chromium concentrations have affected to alite and belite formed (Stephan et al., 1999b). The Ni is not only incorporated into C_3S and C_2S and take up the place of the Ca^{2+} ion. Due to the size of Ni^{2+}ion smaller than Ca^{2+} ion, it does not cause of deformation of C_3S and C_2S lattice (Opoczky and Gavel, 2004), and also the Ni was reacted with Mg in burning process and got $MgNiO_2$ solution in clinker phase

(Stephan et al., 1999b). Moreover, The Zn more easily incorporated in C_3S and concentration of Zn in C_3S also gave higher value than C_2S (Andrade et al., 2003). At 2.0 wt.% of the waste ammunition material which is Cu and Zn had appeared of both alite and belite crystals. Alite was developed in large compact crystals, which tend to appear more prismatic and angular in shape (Kolovos, 2006). Microstructural analysis of the synthesized Portland clinker revealed that the grinding sludge which is contented heavy metals promoted formation of secondary C_2S as well as caused color change of C_3S (Punmatharith et al., 2010).

4.4 The physical properties of clinker at different amounts of heavy metals

4.4.1 Compressive strength

Compressive strength is the capacity of a material or cement mortar to withstand directed pushing forces. The compressive strength is important indicator which is usually obtained experimentally by means of a compressive test. The cubic shape of the cement samples were tested on day 1, day 3, day 7, and day 28 by using compression machine. The strength of these clinker samples were compared with Thai standard no.12/ B.E.2528. Blaine was the one indicator that related to compressive strength which related the fine-grained clinker of grinding machine. It can improve compressive strength in cement mortar. At the Thai standard, the blaine should be $\geq$ 2,800 cm^2/g, but SCCC's standard for OPC type I, the blaine should be $\geq$ 3,300 cm^2/g which was used in this study. Normally, the compressive strength will be increased when the age of sample is increased; however, the results must be compared with the manufacturing standard as shown in Table 4.33. The standard of the compressive strength of 1, 3, 7 and 28 days must be equal or more than 130, 220, 280 and 400 kg/cm^2, respectively.

At high concentration of chromium in clinker, the result showed that it reduced the performance of compressive strength in cement mortar as shown in Table 4.33 and Figure 4.35. The compressive strength of cement mortar that contained 0.1, 0.5, 1.0 and 2.0 wt. % of Cr, at the 1 day test was 111.33, 125.37, 64.59, and 18.03 kg/cm^2, respectively. Whereas, the compressive strength at the 3 days test, was 211.44, 195.20, 121.22, and 70.60 kg/cm^2, respectively. At the 7 days test, the compressive strength was 284.72, 244.17, 151.46, and 140.88 kg/cm^2, respectively. Finally, the compressive strength at the 28 days test, was 366.44, 340.35, 228.78, and

215.11 kg/cm^2, respectively. The results showed that the compressive strength at the 28 days which the clinker contained Cr were lower than 400 kg/cm^2 and were not met the standard. Because when Cr increased, the free lime and C_2S increased, but decreased of C_3S, so it had an effect to the compressive strength. The effect from the Cr in cement mortar was described in previous studies. Murat and Sorrentino (1996) found both 1.2 and 3.25 wt. % of Cr deteriorated the 28 days compressive strength. Stephan, et al. (1999) also found that the compressive strength was reduced at the 2.5 wt % of Cr in cement mortar.

At concentration of nickel in clinker was increased, the result showed that it increased the performance of compressive strength in cement mortar as shown in Table 4.33 and Figure 4.36. The cement mortar contained 0.5% wt. of Ni was given highest compressive strength at 1 day and 28 days, were 138.70 and 417.65 kg/cm^2 respectively, when compared to other ratios of Ni. The compressive strength of cement mortar that contained 0.1, 0.5, 1.0 and 2.0 wt. % of Ni, at the 1 day test was 116.10, 138.70, 127.81, and 119.64 kg/cm^2, respectively. Whereas, the compressive strength at the 3 days test, was 216.34, 261.97, 255.03, and 243.99 kg/cm^2, respectively. At the 7 days test, the compressive strength was 287.71, 315.73, 365.60, and 279.77 kg/cm^2, respectively. Finally, the compressive strength at the 28 days test, was 400.35, 417.65, 415.74, and 404.16 kg/cm^2, respectively. The results showed that the compressive strength at the 28 days which the clinker contained Ni for all ratios were more than 400 kg/cm^2 and were met the standard. Because when Ni increased, the clinker phase and the free lime did not have any effect. So it did not have an effect to the compressive strength as well. From the previous researches, high concentration of Ni can increase compressive strength in cement mortar. Stephan et al (1999) found compressive strength of cement mortar contained 2.5 wt % of Ni higher than control after 28 days test. They also found $MgNiO_2$ from the reaction in burning process can improve the strength due to it reduced concentration of free Mg in the alite.

At concentration of copper in clinker was increased, the result showed that it decreased the performance of compressive strength in cement mortar as shown in Table 4.33 and Figure 4.37. The cement mortar contained 0.1% wt. of Cu was given highest compressive strength at 1 day and 28 days, were 156.68 and 400.48 kg/cm^2 respectively, when compared to other ratios of Cu. At 1.0 and 2.0 wt. % of Cu, have affected the setting time of cement mortar which they have not been set. Because when Cu increased, the free lime and C_2S increased, but decreased of C_3S. The compressive strength of cement mortar that contained 0.1 and 0.5 wt. % of Cu, at the 1 day test was 156.68 and 86.13 kg/cm^2, respectively. Whereas, the compressive strength at the 3 days test, was 225.03 and 210.80 kg/cm^2, respectively. At the 7 days test, the compressive strength was 300.92 and 263.61 kg/cm^2, respectively. Finally, the compressive strength at the 28 days test, was 400.48 and 329.25 kg/cm^2, respectively. The results showed that the clinker contained 0.1 wt.% of Cu improved early strength at the 1 day and the compressive strength at the 28 days which were more than 130 and 400 kg/cm^2 and were met the standard, respectively. Because when Cu increased, the free lime and C_2S increased, but decreased of C_3S, so it had an effect on the compressive strength. From the previous researches, Ma et al. (2006) found that a suitable amount of CuO can lower the clinkering temperature and improve the burn-ability of clinkers. It can also promote the formation of 3CaO·SiO2 and 3CaO·3Al2O3·CaSO4 minerals and facilitate the coexistence of the two minerals in the clinkers. But adding 1% CuO to the raw material can cause the decomposition of 3CaO·3Al2O3·CaSO4.

At concentration of zinc in clinker was increased from 0.1 up to 1.0 wt.%, the result showed that it increased the performance of compressive strength in cement mortar as shown in Table 4.33 and Figure 4.38. The cement mortar contained 0.1 wt.% of Zn was given highest compressive strength at 1 day was 151.79 kg/cm^2 and 1.0 wt.% of Zn was given highest compressive strength at 28 days, was 424.59 kg/cm^2 when compared to other ratios of Zn. The compressive strength of cement mortar that contained 0.1, 0.5, 1.0 and 2.0 wt. % of Zn, at the 1 day test was 151.79, 108.06, 139.66, and 69.10 kg/cm^2, respectively. Whereas, the compressive strength at the 3 days test, was 261.56, 262.38, 260.20, and 178.61 kg/cm^2, respectively. At the 7 days test, the compressive strength was 314.54, 334.57, 330.58, and 215.87 kg/cm^2, respectively. Finally, the compressive strength at the 28 days test, was 401,12, 400.28, 424.59, and 334.67 kg/cm^2, respectively. The results showed that the clinker contained 0.1 and 1.0 wt.% of Zn improved early strength at the 1 day. Because when Zn increased less than 1.0wt.% did not have an effect to the clinker phase and the free lime, so it did not has an effect to the compressive strength as well, but the compressive strength at the 28 days which the clinker contained 2.0 wt.% of Zn were less than 400 kg/cm^2 and were not met the standard. Because when Zn was increased to 2.0wt.%, the free lime and C_2S increased, but decreased of C_3S, so it had an effect to the compressive strength. There is research that related to this situation, Stephan et al. (1999) found at the 1 day at strength test, the compressive strength of cement mortar contained 2.5 wt % of Zn was lower than the control, but after the compressive strength of cement mortar gave the highest values when compared with control and other ratios.

At concentration of combination no. 1 of heavy metals (Ni:Cr:Cu:Zn =1:1:1:1) in clinker was increased from 0.05 up to 0.3 wt.%, the result showed that it increased the performance of compressive strength in cement mortar, but when the concentration of heavy metals more than 0.5 up to 2.0 wt.%, it decreased the performance of compressive strength in cement mortar as shown in Table 4.33 and Figure 4.49. The cement mortar contained 0.05 wt.% of combination of heavy metals was given highest compressive strength at 1 day, 3 days, 7 days and 28 days of 135.19, 241.24, 342.31 and 417.78 kg cm^{-2}, respectively. However, the cement mortar contained 2.0 wt.% of combination of heavy metals was given lowest compressive strength at 1 day, 3 days, 7 days and 28 days of 77.00, 168.67, 239.90 and 345.60 kg cm^{-2}, respectively. The results showed that the clinker contained 0.05 wt.% of combination of heavy metals improved early strength at the 1 day was more than 130 kg cm^{-2} and the compressive strength at the 28 days of the clinker contained 0.05 and 0.3wt.% of combination of heavy metals were more than 400 kg cm^{-2} and were met the standard, respectively. However, when Cu and Cr increased, the free lime and C_2S increased, but decreased of C_3S, so it had an effect on the compressive strength at contained 0.5-2.0wt.% of combination of heavy metals.

At concentration of combination no. 2 of heavy metals (Ni:Cr:Cu:Zn =1:3:5:7) in clinker was increased from 0.05 up to 0.3 wt.%, the result showed that it increased the performance of compressive strength in cement mortar, but when the concentration of heavy metals more than 0.5 up to 2.0 wt.%, it decreased the performance of compressive strength in cement mortar as shown in Table 7. The cement mortar contained 0.05 wt.% of combination of heavy metals was given highest compressive strength at 1 day, 3 days, 7 days and 28 days of 138.98, 251.35, 345.60 and 439.31 kg cm^{-2}, respectively. However, The cement mortar contained 2.0 wt.% of combination of heavy metals was given lowest compressive strength at 1 day, 3 days, 7 days and 28 days of 89.67, 180.93, 240.86 and 331.02 kg cm^{-2}, respectively. The results showed that the clinker contained 0.05 wt.% of combination of heavy metals improved early strength at the 1 day was more than 130 kg cm^{-2} and the compressive strength at the 28 days of the clinker contained 0.05 and 0.3wt.% of combination of heavy metals were more than 400 kg cm^{-2} and were met the standard, respectively. However, when Cu and Cr increased, the free lime and C_2S increased, but decreased of C_3S, so it had an effect to the compressive strength at contained 0.5-2.0wt.% of combination of heavy metals.

The previous researches showed that the effect from the Cr in cement mortar was described which both of 1.2 and 3.25 wt. % of Cr deteriorated the 28 days compressive strength (Murat and Sorrentino, 1996). The compressive strength was reduced at the 2.5 wt % of Cr in cement mortar and the compressive strength of cement mortar contained 2.5 wt % of Ni higher than control after 28 days test and also found $MgNiO_2$ from the reaction in burning process can improve the strength due to it reduced concentration of free Mg in the alite (Stephan et al., 1999b). A suitable amount of CuO can lower the clinkering temperature and improve the burnability of clinkers. It can also promote the formation of 3CaO·SiO2 and 3CaO·3Al2O3·CaSO4 minerals and facilitate the coexistence of the two minerals in the clinkers. But adding 1% CuO to the raw material can cause the decomposition of 3CaO·3Al2O3·CaSO4 (Ma et al., 2006). At the 1 days test, the compressive strength of cement mortar contained 2.5 wt % of Zn lower than control but after the compressive strength of cement mortar gave highest values when compared with control and other ratio (Stephan et al., 1999b). Finally, the residues of metals and metallic oxides incorporated to the clinker during the clinkering process through an alternative fuel (used oils from cars) do not seem to alter detrimentally the characteristics of the material; however, at 3 as well as at 28 days mechanical strengths of M0 (0% w/w of ashes) had lower values than those obtained for the M1-M4 (0.005-0.040% w/w of ashes) (Trezza and Scian, 2000).

Table 4.33: Compressive strength of cement mortar with different ratios of heavy metals.

Description	Blaine (cm^2/g)	1 day (kg/cm^2)	3 day (kg/cm^2)	7 days (kg/cm^2)	28 days (kg/cm^2)
Thai standard	>2800	>85	>120	>150	>245
Manufacturing standard	>3300	>130	>220	>280	>400
Clinker of Manufacturing	3486	131.46	232.83	322.31	410.84
Control clinker	3465	130.13	230.51	307.88	418.47
Cr:1000 ppm	3418	111.33	211.44	284.72	366.44
Cr:5000 ppm	3481	125.37	195.20	244.17	340.35
Cr:10000 ppm	3459	64.59	121.12	151.46	228.78
Cr:20000 ppm	3465	18.03	70.60	140.88	215.11
Ni:1000 ppm	3584	116.10	216.34	287.71	400.35
Ni:5000 ppm	3585	138.70	261.97	315.73	417.65
Ni:10000 ppm	3594	127.81	255.03	365.60	415.74
Ni:20000 ppm	3490	119.64	243.99	279.77	404.16
Cu:1000 ppm	3481	156.68	225.03	300.92	400.48
Cu:5000 ppm	3585	86.13	210.80	263.61	329.25
Cu:10000 ppm	3531	Not set	Not set	Not set	Not set
Cu:20000 ppm	3433	Not set	Not set	Not set	Not set
Zn:1000 ppm	3574	151.79	261.56	314.54	401.12
Zn:5000 ppm	3553	108.06	262.38	334.57	400.28
Zn:10000 ppm	3582	139.66	260.20	330.58	424.59
Zn:20000 ppm	3441	69.10	178.61	215.87	334.67
Ni:Cr:Cu:Zn =1:1:1:1 =500 ppm (125:125:125:125)	3475	135.19	241.24	342.31	417.78
Ni:Cr:Cu:Zn =1:1:1:1 =3000 ppm (750:750:750:750)	3442	124.68	199.72	300.17	400.82
Ni:Cr:Cu:Zn =1:1:1:1 =5000 ppm (1250:1250:1250:1250)	3418	108.19	182.43	252.27	364.28
Ni:Cr:Cu:Zn =1:1:1:1 =10000 ppm (2500:2500:2500:2500)	3424	103.02	194.00	260.06	384.55
Ni:Cr:Cu:Zn =1:1:1:1 =20000 ppm (5000:5000:5000:5000)	3458	77.00	168.67	239.90	345.60
Ni:Cr:Cu:Zn =1:3:5:7 =500 ppm (31.25/93.75/156.25/218.75)	3479	138.98	251.35	345.60	439.31
Ni:Cr:Cu:Zn =1:3:5:7 =3000 ppm (187.50/562.50/937.50/1312.50)	3457	116.37	222.33	308.15	417.52
Ni:Cr:Cu:Zn =1:3:5:7 =5000 ppm (312.5/937.5/1562.5/2187.50)	3455	115.28	194.82	270.96	376.25
Ni:Cr:Cu:Zn =1:3:5:7 =10000 ppm (625/1875/2500/4375)	3408	94.34	197.30	269.21	352.03
Ni:Cr:Cu:Zn =1:3:5:7 =20000 ppm (1250/3750/6250/8750)	3412	89.67	180.93	240.86	331.02

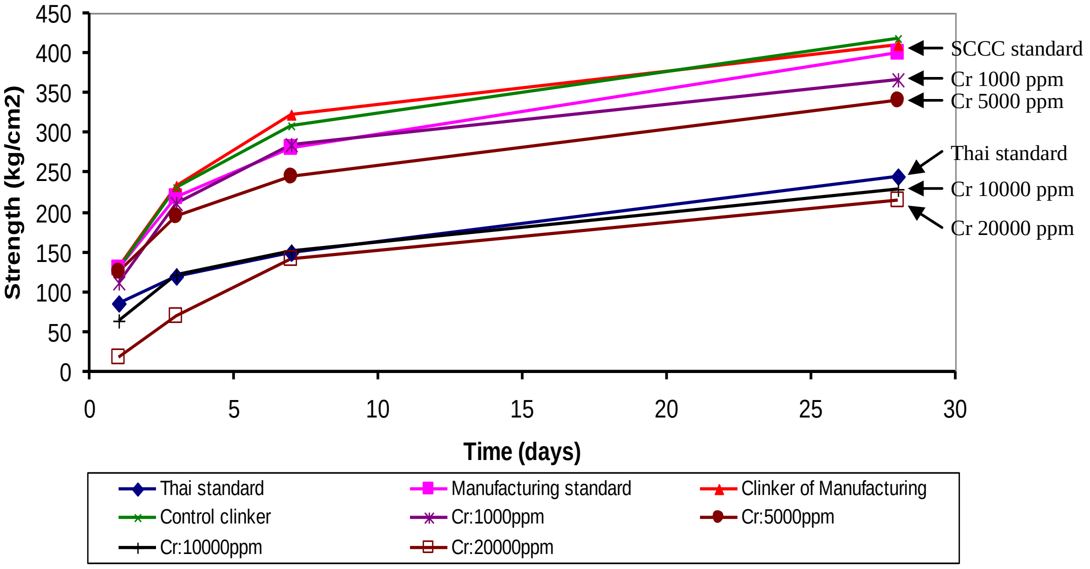


Figure 4.35: Compressive strength of cement mortar with different ratios of Cr concentrations

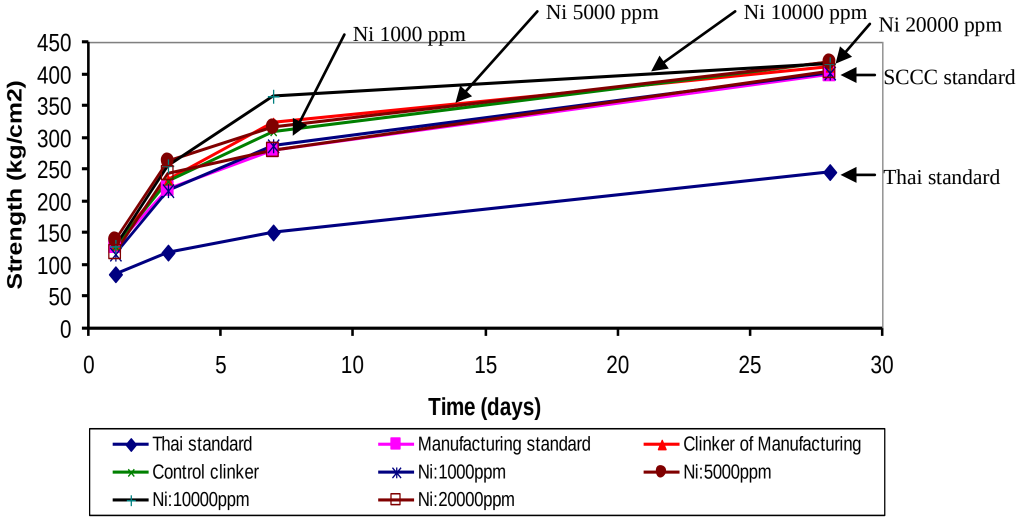


Figure 4.36: Compressive strength of cement mortar with different ratios of Ni concentrations

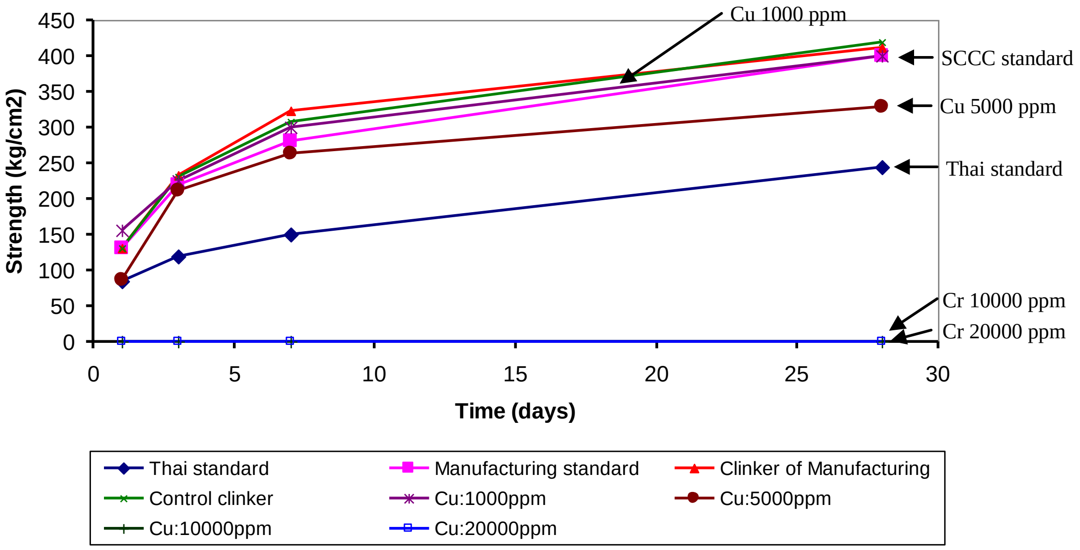


Figure 4.37: Compressive strength of cement mortar with different ratios of Cu concentrations

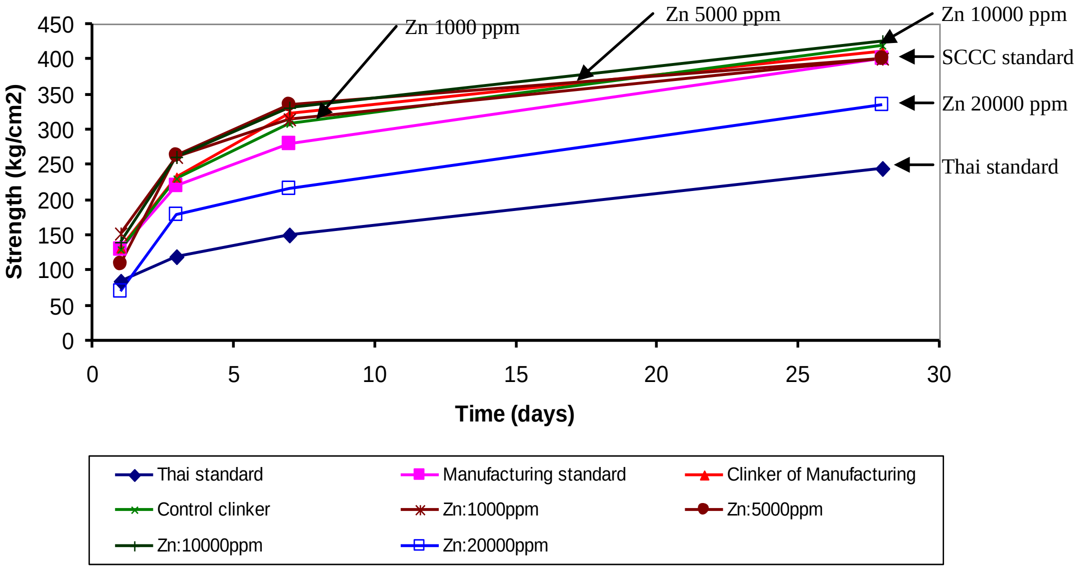


Figure 4.38: Compressive strength of cement mortar with different ratios of Zn concentrations

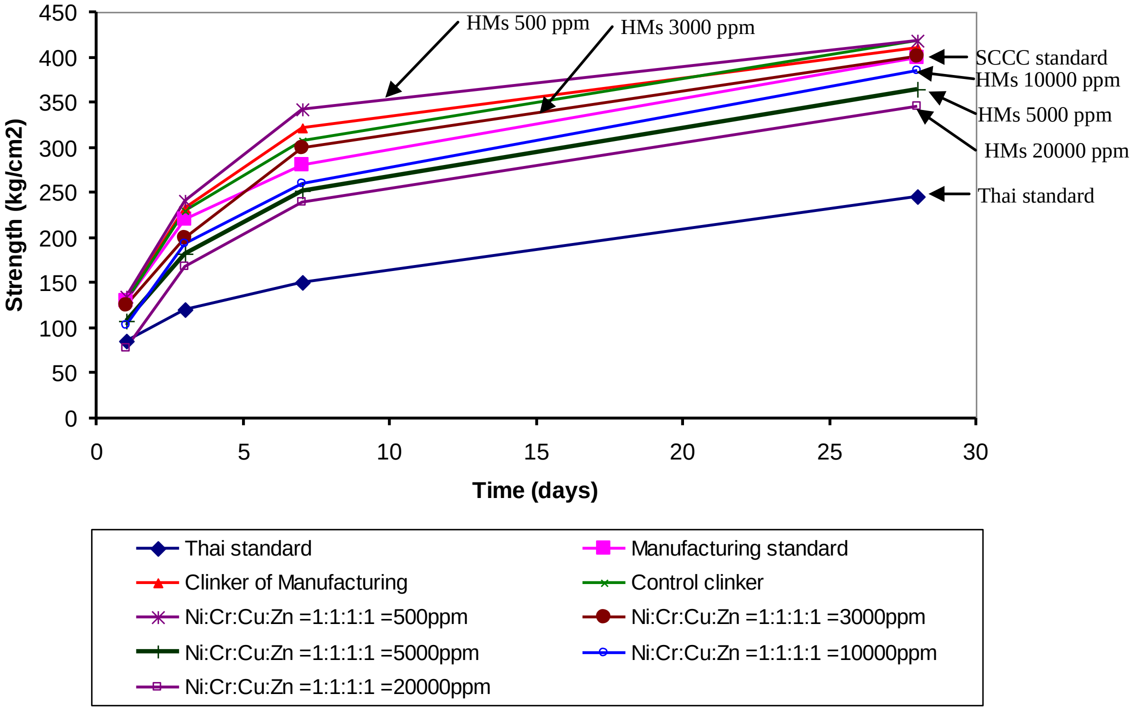


Figure 4.39: Compressive strength of cement mortar with different ratios of the combination concentrations of Ni:Cr:Cu:Zn=1:1:1:1

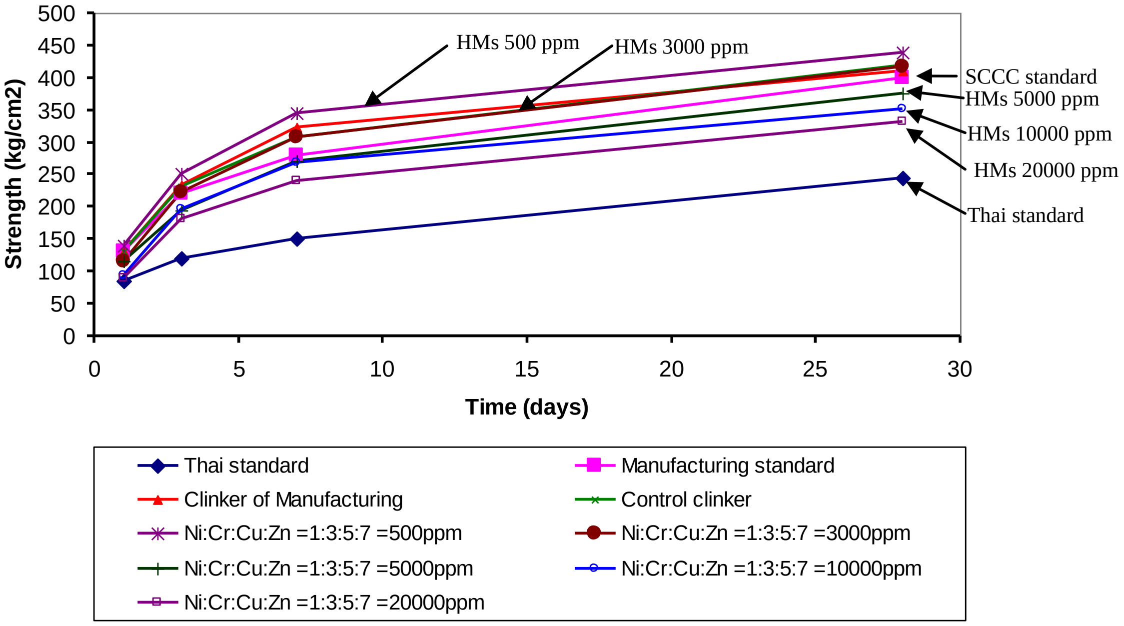


Figure 4.40: Compressive strength of cement mortar with different ratios of the combination concentrations of Ni:Cr:Cu:Zn=1:3:5:7

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the experimental results, it can be concluded that the four types of heavy metals were added to the kiln feed at the different ratios. After the process of burning in the pilot-scale rotary cement kiln, the clinker was produced and experiments were done to determine the effects on the properties of the clinker and cement such as the total concentration of heavy metals in the clinker, leachability, free lime, the color of the clinker, the clinker phase, a crystalline phase of clinker and the compressive strength of cement. The result was analyzed for heavy metals effect on the qualities of the cement and the maximum value related as the following.

The total concentration limits in the clinker, the four types of heavy metals (Cr, Ni, Cu and Zn) which were added to the kiln feed were not destroyed in the burning process and they were trapped in the clinker. The concentration of heavy metals in clinker was higher than in the kiln feed which could be predicted the concentration of each heavy metal by using the linear equations that Cr was used by equations 4.1 to 4.3, Ni was used equations 4.4 to 4.6, Cu and Zn were used the equations 4.7 to 4.9 and 4.10 to 4.12 respectively. The total concentration of heavy metals in the clinker is limited by the standards of the DIW such as Cr is less than 2500 ppm, Ni is less than 2000 ppm, Cu is less than 2500 ppm, and Zn is less than 5000 ppm, so the above equations were used to limit the amount of each heavy metal which could be added into the kiln feed as following.

a. If the sludge waste contains high concentration of each metal, the heavy metal content in the kiln feed such as Cr should be less than 1683 ppm, Ni should be less than 1284 ppm, Cu and Zn should be less than 1678 ppm and 4590 ppm, respectively which the results of total concentration in clinker did not exceed Thai standard such as Cr <2500 ppm, Ni <2000 ppm, Cu <2500 ppm and Zn < 5000 ppm to be classified as non hazardous material.

b. If the sludge waste contain heavy metals in a similar ratio of Ni:Cr:Cu:Zn = 1:1:1:1, so the amount of heavy metals in kiln feed should be limited as follows: Cr should be less than 1666 ppm, Ni should be less than 1166 ppm, Cu should be less than 2314 ppm, and Zn should be less than 4523 ppm in order to the concentration of heavy metals will be limited by the amount of Ni in kiln feed which the results of total concentration in clinker did not exceed Thai standard such as Cr <2500 ppm, Ni <2000 ppm, Cu <2500 ppm and Zn < 5000 ppm to be classified as non hazardous material.

c. If the sludge waste contain heavy metals in a similar ratio of Ni:Cr:Cu:Zn = 1:3:5:7, so the amount of heavy metals in kiln feed should be limited as follows: Cr should be less than 1771 ppm, Ni should be less than 1382 ppm, Cu should be less than 2306 ppm, and Zn should be less than 4737 ppm, so in order to the concentration of heavy metals will be limited by the amount of Cr in kiln feed which the results of total concentration in clinker did not exceed Thai standard such as Cr <2500 ppm, Ni <2000 ppm, Cu <2500 ppm and Zn < 5000 ppm to be classified as non hazardous material.

d. Although at currently the standards of SCCC has controlled the concentrations of heavy metals in the clinker such as Cr <270 ppm, Ni <101 ppm, Cu <280 ppm and Zn <370 ppm to control the qualities of cement as recommended in Holcim Group Companies

Leaching test for heavy metal content increased from 0.05 to 2% by weight was analyzed by WET which the results of both clinker and cement mortar did not exceed Thai standard such as Cr <5 ppm, Ni <20 ppm, Cu <25 ppm and Zn < 250 ppm.

For free lime content (FCaO), the SCCC standard is limited at 1.5%. The amount of Cr increased by 1.0-2.0wt.%, FCaO increased more than 1.5%, so Cr should be less than 0.5wt.%. Same as the amount of Cu increased by 1.0-2.0wt.%, FCaO rapidly increased more than 1.5%, so Cu should be less than 0.5wt.% as well. Although the amount of Ni increased in range 0.1 to 2.0wt.%, FCaO gradually increased still less than 1.5%. Moreover, the amount of Zn has increased, but FCaO slightly decreased lower than the 1.5% and also Zn reduced FCaO. The combination of the four kinds of heavy metals in equal proportions was added in the kiln feed in range 0.05-2.0wt.%, FCaO slightly increased, but it did not exceed 1.5%. Same as the combination of the four kinds of heavy metals in different ratios was added in the kiln feed in range 0.05-2.0wt.%, FCaO was slightly slight increased, but it did not exceed 1.5%.

The heavy metals in the clinker can affect the color of the cement clinker as follows: at 0.5 to 2.0wt.% of Cr, the clinker color were light green and dark green respectively, at 2.0wt.% Ni the clinker becomes dark brown, at 2.0wt.% Cu the clinker becomes brown or light brown, at 2.0 wt.% Zn the clinker becomes brown to dark, At 2.0 wt.% of the combination at similar ratios of heavy metals which the clinker becomes green color, because Cr contained 7000 ppm causes color of clinker as same as at 2.0 wt.% of the combination at similar ratios of heavy metals which the clinker becomes light green as well as Cr contained 5000 ppm affected to color of clinker.

The phase of clinker was analyzed by XRD and SEM-EDX, all heavy metals were incorporated into clinker phase during the burning process. Cr, Cu, Ni and Zn were found and trapped by C_3S, C_2S, C_3A or C_4AF.When Cr increased, has affected on C_3S and C_2S formed, and Cr would inhibit the reaction between C_2S and CaO to form C_3S as well as at Cr 0.5-2.0 wt.% the amount of C_3S decreased less than C_2S, but at Cr <0.5wt.% has not affected clinker phase. Ni was also found and trapped by C_3S, C_2S, C_3A and C_4AF. When Ni increased at 0.1-1wt.%, has not affected clinker phase or C_3S & C_2S formed, but at 2 wt.% Ni C_3S decreased slightly as well as Ni and Mg were reacted to be new form of $MgNiO_2$. When Cu increased, C_3S & C_2S were formed, and Cu would inhibit the reaction between C_2S and CaO to form C_3S as well as at Cu >0.5wt.% the amount of C_3S decreased extremely less than C_2S and C_4AF respectively. When Zn increased more than 1.0-2.0wt.% the amount of C_2S and C_4AF have increased, but C_3S and C_3A were reduced. Zn reacted with Fe, Mn, and Cr to get zinc iron manganese chromium oxide as well as Zn >1.0-2.0wt.% created large size of C_3S. About the combinations of heavy metals, the addition of heavy metals increased in the range of 1.0-2.0%wt., C_2S and C_4AF increased but C_3S was decreased. It was also found that the amount of $C_2S > C_3S > C_4AF$. At 2.0%wt. of combination of heavy metals, can be easily found Cr, Cu, Zn in C_3S, and Cr, Cu, Ni, Zn in C_2S as well as Cr, Zn, Ni in C_4AF.

The compressive strength, the concentration of Cr increased, the compressive strength of cement mortar decreased lower than the standard of SCCC, so the appropriate concentration of Cr that can be mixed in the kiln feed should not exceed 1000 ppm without causing impact on the quality of the cement and the standard concentration in the cement does not exceed standards of the DIW specified. The increased concentrations of Ni resulted in the compressive strength of cement mortar higher than SCCC's standard (min. 130 kg/cm^2 for 1-day and min. 400 kg/cm^2 for 28-day of OPC Type I (bag)), especially at 0.5% wt. of Ni, the compressive strength values at 1 day and 28 days were 138.70 kg/cm^2 and 417.65 kg/cm^2, respectively, so the suitable concentrations of Ni that can be mixed in the KF should not exceed 1166 ppm without causing negative impact on quality of clinker and the standard concentration in the cement do not exceed standards of the DIW specified. The concentrations of Cu were increased, the compressive strengths of cement mortar were lower than the standard of the factory, except that 0.1% wt. of Cu compressive strength values at 1 day and 28 days were 156.68 kg/cm^2 and 400.48 kg/cm^2 respectively, but at Cu 1.0-2.0% wt. have affected the setting time of cement mortar. Therefore, the appropriate concentration of Cu that can be mixed in the KF should not exceed 1678 ppm without causing negative impact on quality of clinker in accordance with the SCCC' standard and the concentration of Cu in the cement does not exceed standards of the DIW specified. When the concentration of Zn increased from 0.1 to 1.0% wt., the results showed that the compressive strength of cement mortar was higher than the factory standard (min. 130 kg/cm^2 for 1-day and min. 400 kg/cm^2 for 28-day of OPC Type I (bag)), especially at 0.1% wt. of Zn compressive strength values at 1 day was 151.79 kg/cm^2 and 1.0% wt. of Zn showed the highest compressive strength at 28 days was 424.59 kg/cm^2, so the appropriate concentrations of Zn that can be mixed in the KF should not exceed 4523 ppm without causing negative impact on quality of clinker in accordance with the SCCC's standard and the concentration in the cement do not exceed standards of the DIW specified. The combination of heavy metals between the Ni:Cr:Cu:Zn was studied, found that at 0.05 to 0.3wt.% the results showed that the compressive strength of cement mortar is higher than the factory standard (min. 130 kg/cm^2 for 1-day and min. 400 kg/cm^2 for 28-day of OPC Type I (bag)) at 28 days were 417.78 kg/cm^2 and 400.82 kg/cm^2 respectively, especially the heavy metals concentration of the mixture was 0.05% wt. has the highest compressive strength at 1 day and 28 days were 135.19 kg/cm^2 and 417.78 kg/cm^2 respectively, so the appropriate concentrations of mixture of heavy metals that can be mixed in the KF should not exceed 3000 ppm without causing negative impact on standards of quality cement factory and the concentration in the cement does not exceed standards of the DIW specified. The concentration of the mixture varied (Ni:Cr:Cu:Zn = 1:3:5:7) of heavy metals increased from 0.05 to 0. 3 wt.% have caused the compressive strength of cement mortar is higher than the factory standard at 28 days were 439.31 kg/cm^2 and 417.31 kg/cm^2, respectively, especially the heavy metals concentration of the mixture was 0.5% wt. has the highest compressive strength at 1 day and 28 days were 138.98 kg/cm^2 and 439.73 kg/cm^2 respectively, so the appropriate concentrations of the heavy metals that can be mixed in the KF should not exceed 3000 ppm without causing negative impact on quality standards of cement and the concentration in the clinker do not exceed standards of the DIW specified.

5.2 Recommendations

1. The effect of heavy metals in setting time, percent residue in different sieves, different thermal gravimetric test were the interesting issues that should be studied.
2. Due to there is a CKD and process water from the burning process, these two wastes should be studied the concentration of heavy metals.
3. Other ratios of heavy metals should be studied, e.g. Ni:Cr:Cu:Zn = 1:2:3:4, Cr:Cu:Zn:Ni = 1:3:5:7 etc.
4. Since the pilot-scale rotary cement kiln was difficult to control temperature and was controlled manually, so it must be run by an expert only. To make it easier to control, the kiln should be improved by adding a heating coil to help increase and maintain a constant temperature and can be run continuous feed.

REFERENCES

Alsop, P.A. 1998. Cement Plant Operations Handbook for Dry Process Plants. 2nd Edition, International Cement Review, Dorking, Surrey (UK).

Andrade, F.R.D., Maringolo, V., Kihara, Y. 2003. Incorporation of V, Zn, and Pb into the crystalline phases of Portland clinker. Journal of cement and concrete Research 33: 63-71.

Anonymous. 2006. Annex 2: The Notification of the Ministry of Industry B.E 2548. Department of Industrial Work [Online]. Available from: http://www2.diw.go.th /PIC/law_01_2.html.

Asavapisit, S. and Chotklang, D. 2004. Solidification of electroplating sludge using alkali-activated pulverized fuel ash as cementitious binder. Journal of cement and concrete Research 34: 349-353.

ASTM C109/C109 M-05. 2005. Standard test method for compressive strength of hydraulic cement mortar (using 2 in or 50 mm cube specimens). ASTM international: 1-9.

Barros, A.M., Espinosa, D.C.R., and Tenorio, J.A.S. 2004. Effect of Cr2O3 and NiO additions on the phase transformations at high temperature in Portland cement. Cement and concrete research 34: 1795-1801.

Bensted, J., and Barnes, P. 2002. Structure and Performance of Cement. 2nd ed., pp. 33-40. New York: Spon Press Publishing.

Bernal, J.D., Jeffery, J.W., Taylor, H.F.W. 1952. Crystallographic research on the hydration of Portland cement: A first report on investigations in progress. Magazine of Concrete Research 3 (11): 49-54.

Brown, L.S. 1948. Long-time study of cement performance in concrete, Chapter 4: Microscopical study of clinkers. J. Amer. Concr. Inst. 44: 877-923.

Cundy, V.A., Lester, T.W., Leger, C., Miller, G., Montestruc, A.N., Acharya, S. and Sterling, A.M. 1989. Rotary kiln incineration-Combustion Chamber Dynamics. Journal of Hazardous Materials 22: 195-219.

Dalton, L. J., Gardner, H. K., Seager, P. S., Weimer, L. M., Spear, C.M. J., Magee, J. B. 2004. Properties of Portland cement made from contaminated sediments. Resources Conservation and Recycling 41: 227-241.

Denise, D.R., Espinosa, Jorge, Tenorio, A.S. 2000. Laboratory study of galvanic sludge's influence on the clinkerization process. Resources conservation & recycling 31: 71-82.

Diane Drew, RN, MPA; Ifeoma Stella Izuchukwu, MD; and Pamela Tucker, MD. 1992. Case Studies in Environmental Medicine (CSEM) Chromium Toxicity. Agency for toxic substance and disease registry, Department of health and human sevice.

Environmental Science & Engineering Inc. 1991. Evaluation of Acceptable Levels of Trace Elements in Portland Cement, U.S.A.

Environmental Toxicology International Inc. 1992. All Fired Up Burning Hazardous Waste In Cement Kilns. Washington, U.S.A.

Fluka Chemie GmbH, 2003/2004. Scientific research. A.C.S. Xenon Limited Partnership, Bangkok, Thailand.

Gougar, M.L.D., Scheetz, B.E. and Roy, D.M. 1996. Ettringite and CSH Portland cement phases for waste ion immobilization: A review. Journal of Resource, Conservation, and Recycle. ELSEVIER: 71-82.

Guo, Q., Eckert, Jr., and James, O. 1996. Heavy metal outputs from a cement kiln co-fired with hazardous waste fuels. Journal of Hazardous Materials 51: 47-65.

Hewlett, P.C. 1998. Lea's Chemistry of Cement and Concrete. 4th ed., pp. 57-87. Arnold, London, Great Britain.

Holcim, and GTZ. 2006. Guideline on co-processing waste material in cement production, pp. 13-15. The GTZ-Holcim Public, Germany.

Kaantee, U., Zevenhoven, R., Backman, R., and Hupa, M. 2000. The impact of alternative fuels on the cement manufacturing process. Proceedings of R'2000 Recovery-recycling-reintegration Canada: 1070-1075.

Kakali, G., Parissakis, G., and Bouras, D. 1996. A study on the burnability and the phase formation of PC clinker containing Cu oxide. Cement and Concrete Research 26: 1473-1478.

Kasprzak, K., Sunderman J., and Salnikow, K. 2003. Nickel carcinogenesis. Journal of Mutation Research: 67-97.

Knofel, D. 1978. Beeinflussung einiger Eigenschaften des Portlandzementklinkers und des Portlandzementes durch ZnO und ZnS. Zement-Kalk-Gips 31:157-161.

Kolovos, K., Barafaka, S., Kakali G., and Tsivilis S. 2005. CuO and ZnO addition in the cement raw mix: effect on clinkering process and cement hydration and properties. Ceramics-Silikáty 49 (3): 205-212.

Kolovos, K., Tsivilis, S., and Kakali, G. 2002. The effect of foreign ions on the reactivity of the CaO-SiO2-Al2O3-Fe2O3 system Part II: Cations. Journal of cement and concrete Research 32: 463-469.

Lea, F., and Garston, P.T. 1935. Building Research Establishment. Building Research Technical Paper no. 16. UK.

Lemieux, P., Stewart, E., Realff, M., and Mulholland, J.A. 2004. Emissions study of co-firing waste carpet in a rotary kiln. Journal of Environmental Management 70: 27-33

Li, X.D., Zhang, Y.M., Poon, C.S. and Lo, I.M.C. 2001. Study of zinc in cementitious material stabilized/solidified wastes by sequential chemical extraction and microstructural analysis. Chemical Speciation and Bioavailability 13 (1): 1-7.

Ma, S., Shen, X., Gong, X., and Zhong, B. 2006. Influence of CuO on the formation and coexistence of $3CaO{\cdot}SiO_2$ and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ minerals. Cement and Concrete Research 36: 1784-1787.

Malozhon, L.I., Butt, Y.M., and Timashev, V.V. 1971. Properties of cements prepared from chromium containing raw meal (in Russian). Tr Mosk Khim-Tekhnol Inst. 68: 160-163.

Mindess, S., Young, J.F., and Darwin, D. 2003. Concrete. 2nd ed. Prentrice Hall.

Mokrzycki, E., and Uliasz B.A. 2003. Alternative fuels for the cement industry. Applied Energy 74: 95–100.

Murat, M., and Sorrentino, F. 1996. Effect of large additions of Cd, Pb, Cr, Zn, to cement raw metal on the composition and the properties of the clinker and the cement. Cement and Concrete Research 26: 377-385.

Neville, A.M. 2003. Properties of concrete. 4th ed. Prentice Hall.

Odler, I., and Schmidt, O. 1980. Structure and properties of Portland cement clinker doped with zinc oxide. J-Am Ceram Soc 63: 13-16.

Opoczky, L., and Gavel, V. 2004. Effect of certain trace elements on the grindability of cement clinkers in the connection with the use of wastes. International journal of mineral processing 748: 126-136.

Peray, K.E. 1986. The rotary cement kiln. 2nd ed. pp. 87, 139, 148-151. Chemical Publishing Co., Inc. New York, U.S.A.

Polat, R., Gurol, A., Budak, G., Karabulut, A., and Ertugrul, M. 2004. Elemental composition of cement kiln dust, raw material and cement from a coal-fired cement factory using energy dispersive X-ray fluorescence spectroscopy. Journal of Quantitative Spectroscopy & Radiative Transfer 83: 377-385.

Prodjosantoso, A.K., and Kennedy, B.J. 2003. Heavy metals in cement phases: on the solubility of Mg, Cd, Pb and Ba in $Ca_3Al_2O_6$. Cement and Concrete Research 33: 1077–1084.

Punmatharith, T., Rachakornkit, M., Imyim, A., and Wecharatana, M. 2010. Co-processing of Grinding Sludge as Alternative Raw Material in Portland Cement Clinker Production. Journal of Applied Sciences 10: 1525-1535.

Rachakornkij, M. 2000. Utilization of municipal solid waste incinerator fly ash in cement mortars, Doctoral Dissertation. Department of Civil and Environmental Engineering, New Jersey Institute of Technology.

Ract, P.G., Espinosa, D.C.R, and Tenorio, J.A.S. 2003. Determination of Cu and Ni incorporation ratios in Portland cement clinker. Waste Management 23: 281-285.

Richaud, R., Herod, A.A., and Kandiyoti, R. 2004. Comparison of trace elements in low- temperature and high-temperature ash from coals and biomass. Fuel 83: 2001-2012.

Shih, P., Chang, J., Lu,H., and Chiang, L. 2005. Reuse of heavy metal-containing sludges in cement production. Cement and Concrete Research 35: 2110 – 2115.

Sinyoung, S., Songsiriritthigul, P., Asavapisit, S., and Kajitvichyanukul, P. 2011. Chromium behavior during cement-production processes: A clinkerization, hydration, and leaching study. Journal of Hazardous Materials 191: 296-305.

Sorrentino, F.P. 1998. Dicalcium silicate in special cement. Proc. 20th Int. Conf. Cem. Micr, Guadulajara.

Sprung, S. 1985. Technological Problems in Pyroprocessing Cement Clinker; Cause and Solution. 1st ed. Beton-Verlag, Dusseldorf.

Stephan, D., Mallmann, R., Knofel, D., and Hardtl, R. 1999a. High intakes of Cr, Ni, and Zn in clinker Part I: Influence on burning process and formation of phases, Cement and Concrete Research 29: 1949-1957.

Stephan, D., Mallmann, R., Knofel, D., and Hardtl, R. 1999b. High intakes of Cr, Ni, and Zn in clinker Part II: Influence on burning process and formation of phases. Cement and Concrete Research 29: 1959-1967.

Taweekitwanit, E. 2004. Leaching Behavior of Heavy Metals from Cement Derived from The Co-Burning of Hazardous Waste. Master’s Thesis. Graduate School, Chulalongkorn University.

Taylor, H.F.W. 1990. Cement Chemistry, pp. 1, 2, 65, 66, 69, 96. Academic Press, New York.

Trezza, M.A., and Scian, A.N., 2000. Burning wastes as an industrial resource their effect on Portland cement clinker. Cement and Concrete Research 30: 137–144.

Trezza, M.A., and Scian, A.N., 2005. Waste fuels: their effect on Portland cement clinker. Cement and Concrete Research 35: 438–444.

U.S. Environmental Protection Agency (U.S. EPA). 1991. Burning of hazardous waste in boilers and industrial furnaces, Final rule Federal Register. (February 21); 56:7134-7240. U.S.A.

Vincoli, W.J. 1997. Risk Management for Hazardous Chemicals V.1 and V.2, pp. 649. CRC Press Inc.

Von, S.M., and Tompkins, J.B. 1991. Metal emissions are predictable. Rock Products April: 31-35.

Wang, S., and Vipulanandan, C. 2000. Solidfication/stabilization of Cr(VI) with cement Leachability and XRD analyses. Cement and Concrete Research 30 (3): 385-389.

Welch, J.H., and Gutt, W. 1959. Tricalcium silicate and its stability with in the system $CaO-SiO_2$. Journal of the American Ceramic Society 42: 11-15.

APPENDICES

APPENDIX A

Figure A.1: The pilot-scale rotary cement kiln

Figure A.2: The pilot-scale rotary cement kiln which can be lifted to remove the clinker inside the kiln

Figure A.3: The pilot-scale rotary cement kiln with all equipments

Figure A.3: The cooling tower

Figure A.4: The two LPG burners were used for heating in the kiln

Figure A.5: The new casting cement inside the kiln with low-cement castable type: D59A

Figure A.6: The sample before burning in the pilot-scale rotary cement kiln

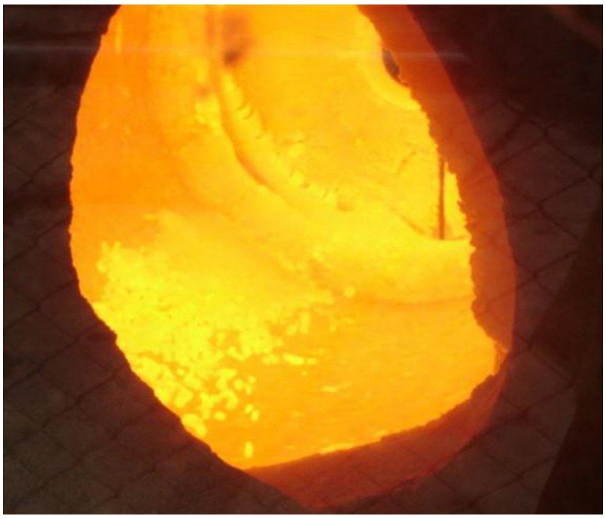
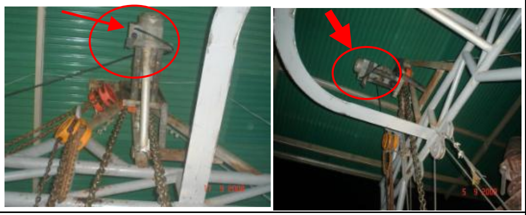


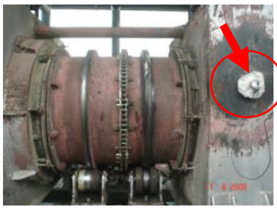
Figure A.7: The sample was burning in the pilot-scale rotary cement kiln

Figure A.8: The clinker after burning in the pilot-scale rotary cement kiln

Figure A.9: The reparation of the pilot-scale rotary cement kiln for casting new cement inside the kiln with low-cement castable type: D59A

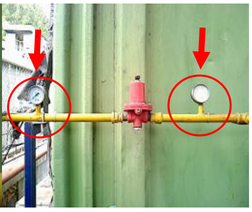
Table A1: The equipment lists of the pilot scale rotary cement kiln.

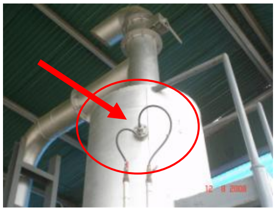
Item	Description	Unit	Position	Picture
1	Hoist for lifting, capacity 5 tons	1	On top of the kiln for lifting the kiln	
2	Hoist for lifting, capacity 2.5 tons	2	On top of the kiln for lifting the kiln	
3	Hoist for lifting, capacity 2 tons	1	On top of the kiln for lifting loading chute	
4	Aluminum ladder	1	Put on the ground, in front of the kiln	
5	Steel ladder	1	Put on the ground, in front of the kiln	
6	Stainless steel loading chute	2	Put on the ground, beside the kiln	
7	Steel loading chute	6	Keep in container room	

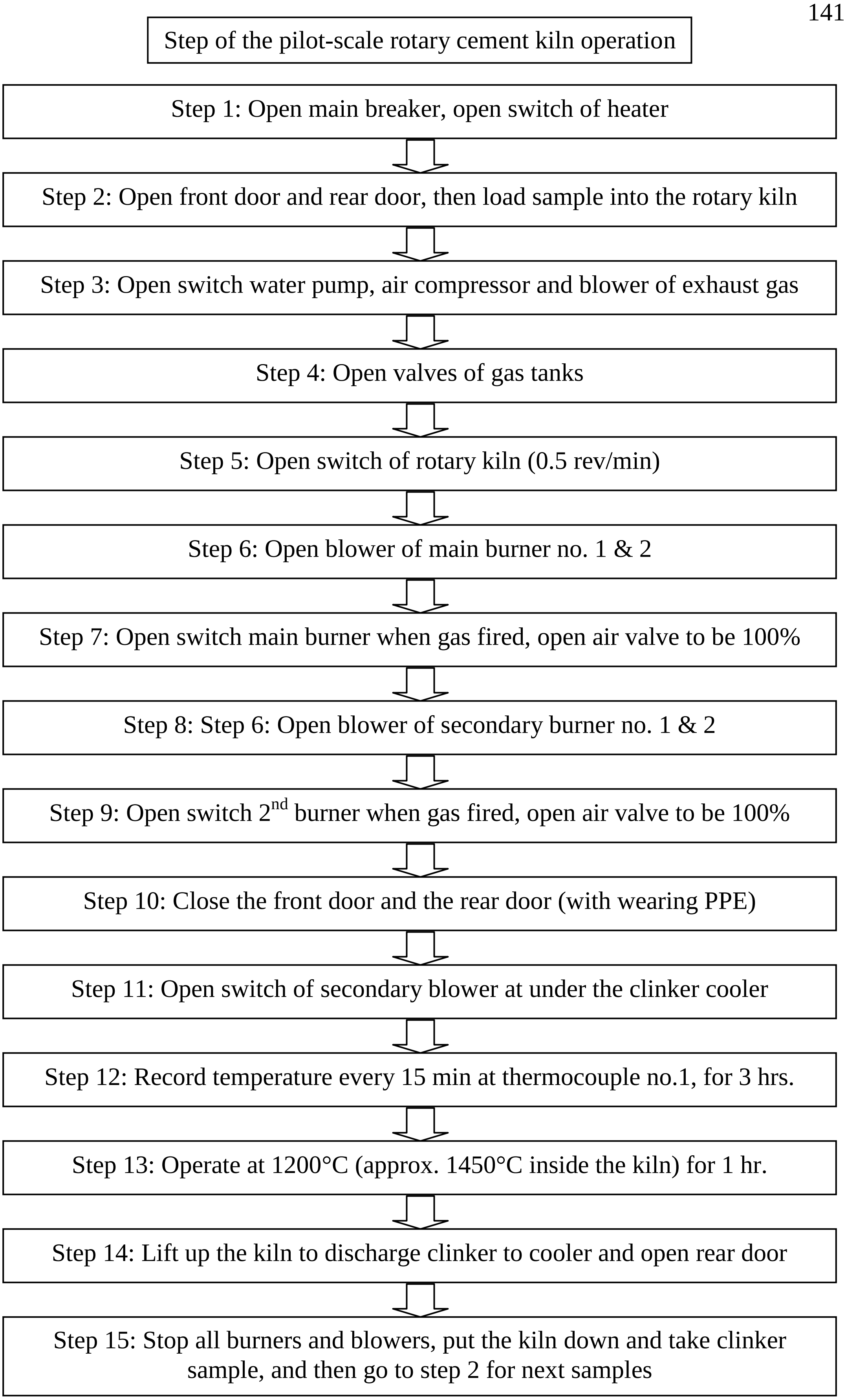
8	Motor, 1hp.	1	Beside rotary kiln	 
9	Air blower for clinker cooler	1	Beside the kiln, under clinker cooler	 
10	Air blower for the cooling tower	1	Beside the cooling tower	 
11	Thermocouple type R	1	Beside the hot air outlet chamber	 
12	Thermocouple type R	1	Behide the kiln in clinker cooler	
13	Steel tray for clinker collection	2	In the clinker cooler	 
14	Water tank capacity 1000 liters	1	On the ground in the corner	 
15	Water pump	1	Beside water tank	

16	Air compressor	1	Beside water pump	 
17	Main control cabinet for the kiln (to control motor, blowers, air compressor, water pump)	1	Backside the kiln	
18	Burner control cabinet for the kiln	1	Backside the kiln, beside main control cabinet	
19	Hoist control cabinet for lifting the kiln	1	Backside the kiln, beside burner control cabinet	
20	Motor speed reducer	1	Backside the kiln, beside hoist control cabinet	
21	Blower high pressure	1	On the ground backside the kiln of clinker cooler	 
22	Blower low pressure	2	On the ground backside the kiln of clinker cooler	 
23	Gas detectors	2	Backside the kiln on the gas pipe line	

24	Gas emergency switch off	1	Backside the kiln on the gas pipe line	
25	Gas tanks (45 kg)	9	Backside the kiln	
26	Heater	1	Backside the kiln in water tray	 
27	Water tray for heating gas tanks	1	On the ground backside the kiln	
28	Fire extinguishers	3	On the wall backside the kiln 2 units and 1 units in the front	
29	Sport lights	2	Backside the kiln 1 units and 1 units in the front	 
30	Fluorescent lamps	4	Backside the kiln 2 units and 2 units on top of the kiln	
31	Table steel	1	Backside the kiln	

32	Plastic chairs	4	In container room	
33	LPG Burners	2	Inside the kiln	
34	Harrow steel for sweeping the clinker	2	Backside the kiln	
35	Gas pressure gates	3	Backside the kiln on the gas pipe line	 
36	Solenoid valve	2	Backside the kiln on the gas pipe line	 
37	Gas pressure adjustment	1	Backside the kiln on the gas pipe line	 
38	Gas pressure reducer	2	Backside the kiln on the gas pipe line	 
39	Wastewater collection tray	1	On the ground beside the cooling tower	

40	Water nozzle	1	On the cooling tower	



Step of the pilot-scale rotary cement kiln operation

Step 1: Open main breaker, open switch of heater

Step 2: Open front door and rear door, then load sample into the rotary kiln

Step 3: Open switch water pump, air compressor and blower of exhaust gas

Step 4: Open valves of gas tanks

Step 5: Open switch of rotary kiln (0.5 rev/min)

Step 6: Open blower of main burner no. 1 & 2

Step 7: Open switch main burner when gas fired, open air valve to be 100%

Step 8: Step 6: Open blower of secondary burner no. 1 & 2

Step 9: Open switch 2nd burner when gas fired, open air valve to be 100%

Step 10: Close the front door and the rear door (with wearing PPE)

Step 11: Open switch of secondary blower at under the clinker cooler

Step 12: Record temperature every 15 min at thermocouple no.1, for 3 hrs.

Step 13: Operate at 1200°C (approx. 1450°C inside the kiln) for 1 hr.

Step 14: Lift up the kiln to discharge clinker to cooler and open rear door

Step 15: Stop all burners and blowers, put the kiln down and take clinker sample, and then go to step 2 for next samples

Figure A.10: Steps of the pilot-scale rotary cement kiln operation

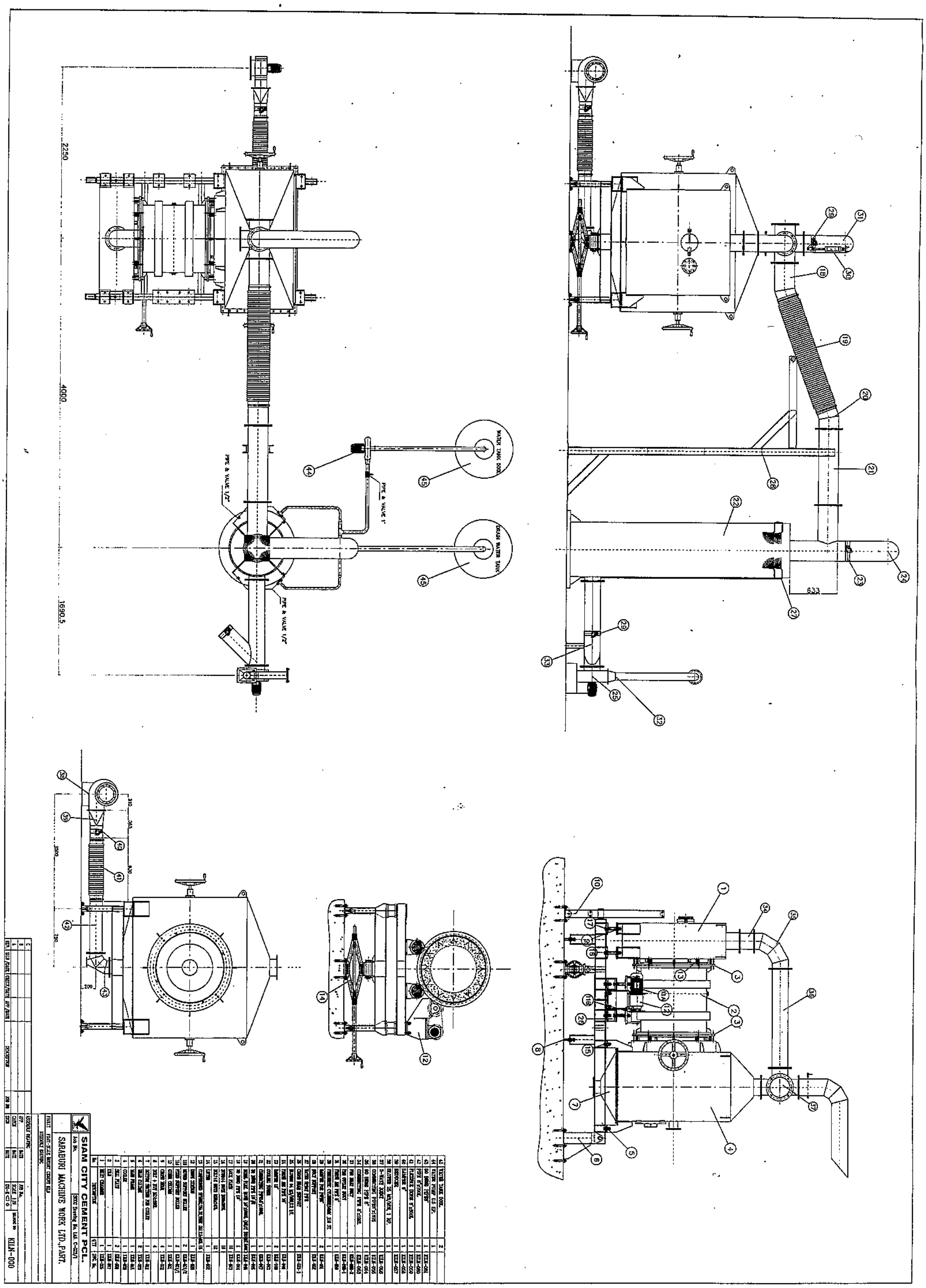


Figure A.11: The pilot-scale rotary cement kiln assembly drawing

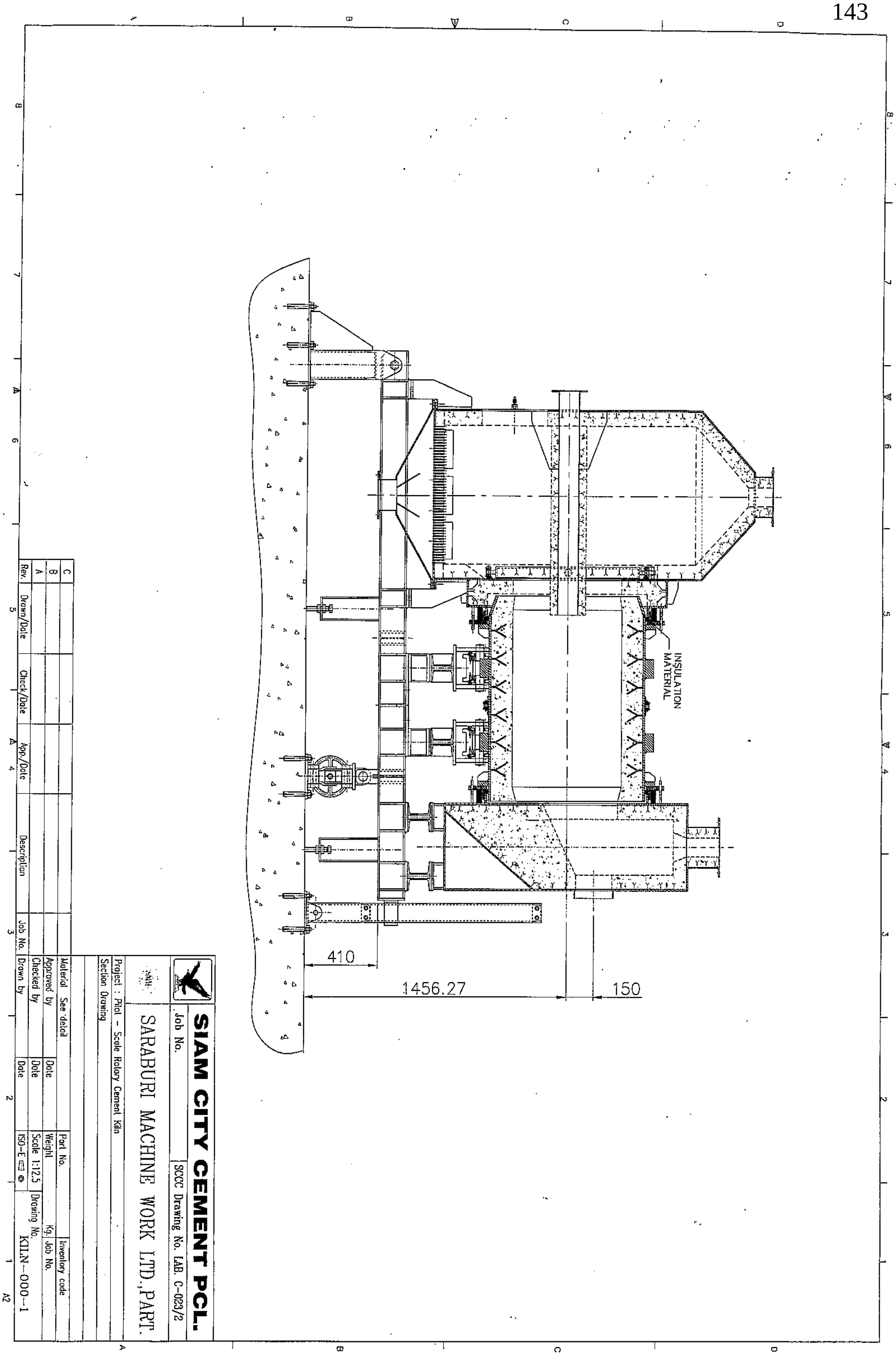


Figure A.12: Section view of the pilot-scale rotary cement kiln

APPENDIX B

Sample preparations and instruments of analysis

Figure B.1: Chromium (III) oxide

Figure B.2: Copper (II) oxide

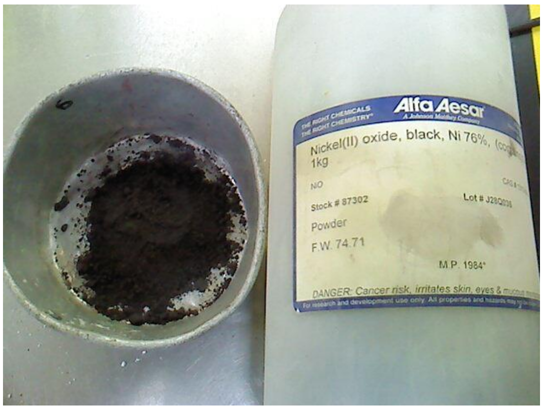


Figure B.3: Nickel (II) oxide

Figure B.4: Zinc oxide

Figure B.5: Kiln feed after pre-calcinations

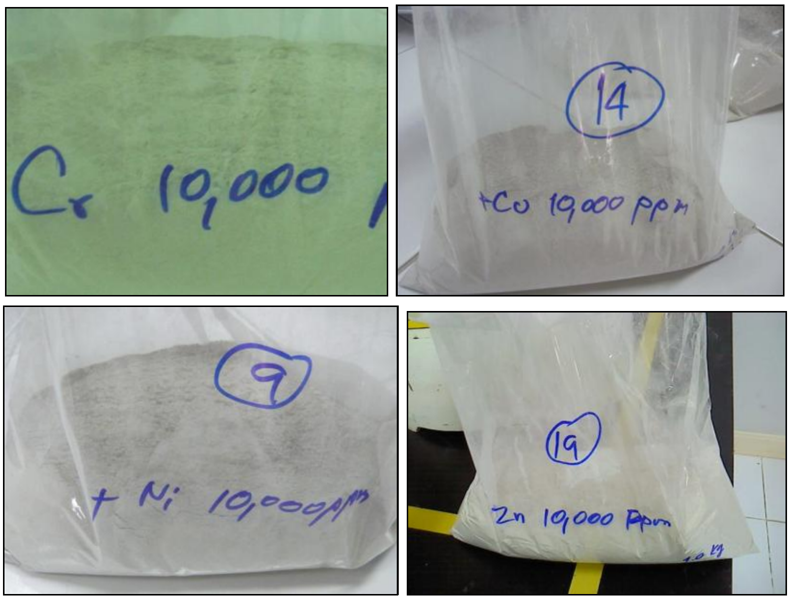


Figure B.5: Examples of kiln feed were added each heavy metal at 10000 ppm

Figure B.6: Examples of kiln feed were added combination of heavy metals

Figure B.7: The mixtures were made to be pieces and then sent to oven

Figure B.8: The clinker after burning by the pilot-scale rotary cement kiln

Figure B.9: Blaine testing equipment and digital scales

Figure B.10: Sieve machine and V-mix machine

Figure B.11: Oven for sample preparations

Figure B.12: Jaw crusher for crushing clinker

Figure B.13: Sieve no.8, 2.36 millimeters was used to sieve crushed clinker before sending to lab ball mill machine

Figure B.14: Lab ball mill machine

Figure B.15: Cement mortar mixing machine

Figure B.16: Cement mortar in the molds

Figure B.17: Cement mortar were kept at moisture control room

Figure B.18: Compression machine

Figure B.19: Microwave digestion machine

Figure B.20: Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Figure B.21: The swinging mill machine

Figure B.22: Tablet pressing machine

Figure B.23: The combination machine of XRF and XRD

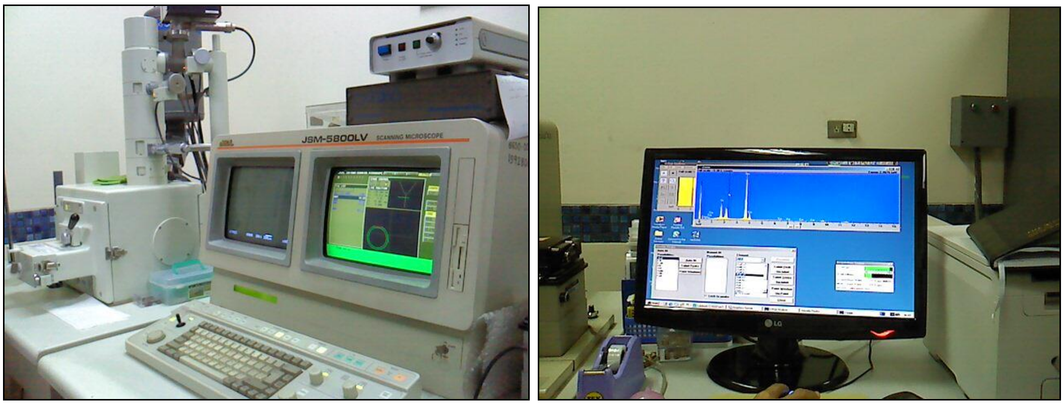


Figure B.24: Scanning Electron Microscope (SEM)

APPENDIX C

NOMENCLATURE

ASTM = American Society for Testing and Materials
C_2S = Dicalcium silicate
C_3S = Tricalcium silicate
C_3A = Tricalcium aluminite
C_3AF = Tetracalcium aluminoferrite
Cr = Chromium
Cu = Copper
FCaO = Free lime
ICP = Inductively coupled plasma optical emission spectroscopy
LOI = Loss on iginition(%) defined by ASTM C311 as the weight fraction of materials that is lost by heating the oven dried sample at 750 °C
M3052 = Microwave assisted acid digestion of siliceous and organically based matrice (U.S. EPA method 3052)
ND = Non detectable
Ni = Nickel
OPC Type I = Ordinary Portland Cement Type I
PPE = Personal Protective Equipment
RCRA = Resource Conversation and Recovery Act
SEM = Scanning electron microscopy
TTLC = Total Threshold Limit Concentration
TC = Total Concentration
STLC = Soluble Threshold Limit Concentration
TCLP = Toxicity Characteristic Leaching Procedure
XRD = X-ray Diffractometer
XRF = X-ray fluorescence spectrometry
W.E.T. = Waste Extraction Test
Zn = Zinc

APPENDIX D

Table D.1: Summary of the effect of heavy metals to the clinker properties.

Heavy Metal (HM)	TC and WET by ICP	Free lime	Color of clinker	Phase of clinker by XRF and XRD	Phase of clinker by SEM	Compressive strength	Suitable conc. of HM in KF
Cr	-TC, DIW std. < 2500ppm - TC, SCCC std. <270ppm - Cr was not destroyed in burning process and occurred in clinker. - Cr conc. in CL > KF - Y_{Cr}=1.4388X_{Cr}+78.42 (4.1) Cr in combination I (1:1:1:1); - Y_{Cr} = 1.4538X_{Cr} + 78.42 (4.2) Cr in combination II (1:3:5:7); - Y_{Cr} = 1.3676X_{Cr} + 78.42 (4.3) - WET, conc. Cr in CL & Mortar were not over standard (<5ppm)	- Cr↑, FCaO↑ - 0.1-0.5%wt.Cr,FCaO=1.26 & 1.12 < 1.5% OK. - 1.0%wt.Cr, FCaO↑2.82% - 2.0%wt.Cr, FCaO↑2.22% - FCaO, SCCC std. <1.5%	- 0.5% wt. Cr light Green - 2%wt.Cr Dark green	-Cr↑ have affected to C_3S & C_2S formed. -Cr <0.5wt.% no affects to clinker phase. -Cr 0.5-2%wt. C_3S↓, C_2S> C_3S (XRD) - New compounds were found $Ca_4A16O_{12}Cr_4$, $Ca_6A14Cr_2O_{15}$ - Cr would inhibit the reaction between C_2S & CaO to form C_3S.	- Cr was found & trapped by C_3S & C_2S, C_3A & C_4AF.	- Follow SCCC std. - Blaine std. > 3300, 3400±100 cm^2/g - Strength std. 1, 3, 7, 28d =130, 220, 280, 400kg/cm^2, respectively. - Cr↑, strength↓ - The highest strength at 0.1%wt.Cr was 1d = 111.33 kg/cm^2, 28d =366.44 kg/cm^2 - All ratios of Cr in clinker were not met standard (<400 kg/cm^2)	Cr<1000ppm
Ni	-TC, DIW std. < 2000ppm - TC, SCCC std. <101ppm - Ni was not destroyed in burning process and occurred in clinker. - Ni conc. in CL > KF - Y_{Ni}=1.5266X_{Ni}+39.34 (4.4) Ni in combination I (1:1:1:1); - Y_{Ni} = 1.6817X_{Ni} + 39.34 (4.5) Ni in combination II (1:3:5:7); - Y_{Ni} = 1.4188X_{Ni} + 39.34 (4.6) - WET, conc. Ni in CL & Mortar were not over standard (<20ppm)	- Ni↑, FCaO↑ increased slightly but not over std. - 0.1-2.0%wt.Ni, < 1.5% OK. - 0.1%wt.Ni, FCaO=0.5% - 2.0%wt.Ni, FCaO=1.0% - FCaO, SCCC std. <1.5%	- 2%wt.Ni Dark brown (the color of clinker becomes dark brown)	- Ni↑ 0.1-1% has no affected to clinker phase or C_3S & C_2S formed. - Ni 2%wt., %C_3S↓ slightly decreased. - Ni & Mg were reacted to be new form is $MgNiO_2$.	- Ni was found & trapped by C_3S & C_2S, C_3A & C_4AF.	- Ni↑increased, increased the performance of compressive strength. - 0.5%wt.Ni was given highest strength 1 d & 28 d = 138.70 & 417.65 kg/cm^2, respectively. - All ratios of Ni were met standard of SCCC (>400 kg/cm^2).	Ni<1000ppm
Cu	-TC, DIW std. < 2500ppm - TC, SCCC std. <280ppm - Cu was not destroyed in burning process and occurred in clinker. - Cu conc. in CL > KF - Y_{Cu}=1.4118X_{Cu}+130.94 (4.7) Cu in combination I (1:1:1:1); - Y_{Cu} = 1.0238X_{Cu} + 130.94 (4.8) Cu in combination II (1:3:5:7); - Y_{Cu} = 1.0275X_{Cu} + 130.94 (4.9) - WET, conc. Cu in CL & Mortar were not over standard (<25ppm)	- Cu↑, FCaO↑ rose extremely. - 0.1-0.5%wt.Cu,FCaO<1.5% - 1.0-2.0%wt.Cu, FCaO> 1.5% - 1.0%wt.Cu, FCaO=11.46% - 2.0%wt.Cu, FCaO=12.70% - FCaO is very high, made clinker not set form completely & make the cement can brake easily. - FCaO, SCCC std. <1.5%	- 2%wt.Cu Back to Tan (brown or light brown)	-Cu↑ have affected to C_3S & C_2S formed. -Cu >0.5wt.% affected to clinker phase, C_3S↓ decreased extremely, -Cu >1.0-2.0wt.% found that C_2S> C_4AF > C_3S (XRD). - Cu made the effect into alite phase and Cu can inhibit the C_2S to change into C_3S form.	- Cu was found & trapped by C_3S & C_2S, and found in C_3A & C_4AF.	-Cu↑, strength↓ -0.1%wt.Cu improved early strength and was given highest compressive strength at 1 d & 28 d = 156.68 & 400.48 kg/cm^2, respectively. -1.0-2.0%wt.Cu cement could not be set, so it have affected to the setting time of cement mortar.	Cu<1000ppm

Zn	-TC, DIW std. < 5000ppm - TC, SCCC std. <370ppm - Zn was not destroyed in burning process and occurred in clinker. - Zn conc. in CL > KF - $Y_{Zn}=1.0394X_{Zn}+229.56$ (4.10) Zn in combination I (1:1:1:1); - $Y_{Zn} = 1.0548X_{Zn} + 229.56$ (4.11) Zn in combination II (1:3:5:7); - $Y_{Zn} = 1.007X_{Zn} + 229.56$ (4.12) - WET, conc. Zn in CL & Mortar were not over standard (<250ppm)	- Zn↑, FCaO↓ decreased slightly (0.89 reduce to 0.83<1.5% OK.) - 2.0%wt.Zn, FCaO=0.83%. - Zn can be improved %FCaO - FCaO, SCCC std. <1.5%.	- 2%wt.Zn brown to dark	- Zn >1.0-2.0wt.% found that C_2S↑, C_4AF ↑ but reduce C_3S and C_3A (XRD). - Zn reacted with Fe, Mn, and Cr to get zinc iron manganese chromium oxide (Zn [$Fe_{0.5}Mn_{0.5}Cr$]O_4).	- Zn >1.0-2.0wt.% created large size of C_3S. - Zn was found & trapped by C_3S & C_2S, and found in C_4AF.	- Zn↑increased (0.1-1.0%wt), increased the performance of compressive strength (>400 kg/cm^2). - 0.1%wt.Zn was given highest early strength 1 d = 151.79 - 1.0%wt.Zn was given highest strength 28 d = 424.59 kg/cm^2, - 2.0%wt.Zn, strength↓ was reduced at 28 d = 334.67 kg/cm^2,	Zn<5000ppm
Ni:Cr: Cu:Zn 1:1:1:1	- All heavy metals (HM) occurred in clinker. - $Y_{Ni} = 1.6817X_{Ni} + 39.34$ (4.5) - $Y_{Cr} = 1.4538X_{Cr} + 78.42$ (4.2) - $Y_{Cu} = 1.0238X_{Cu} + 130.94$ (4.8) - $Y_{Zn} = 1.0548X_{Zn} + 229.56$ (4.11) - WET, conc. HM in CL & Mortar were not over standard.	- HM↑, FCaO↑ gradually increased but not over std. - 0.05-2.0%wt.HM, FCaO range 0.88-1.21% <1.5% OK. - FCaO, SCCC std. <1.5%.	- 2%wt.HM Green, because Cr contained 7000 ppm affected to color of clinker.	- 1.0-2.0%wt.HM, C_2S↑, C_3S↓ found that C_2S> C_3S > C_4AF (XRD). - At 2.0%wt. HM, C_4AF↑.	- At 2.0%wt.HM found that HM occurred in C_3S-Cr, Cu, Zn C_2S-Cr, Cu, Ni C_4AF-Cr, Zn, Ni - All HMs were incorporated into clinker phase during the burning process.	- 0.05-0.3%wt. HM , strength ↑ > 400 kg/cm^2 (417.78 and 400.82 kg/cm^2, respectively). - 0.5-2.0%%wt. HM , strength ↓ < 400 kg/cm^2. - 0.05%wt.HM was given highest compressive strength at 1 d & 28 d = 135.19 & 417.78 kg/cm^2, respectively. - 2.0%wt.HM, strength↓ was reduced at 28 d = 345.60 kg/cm^2,	Combination of Ni:Cr:Cu:Zn = 1:1:1:1 < 3000 ppm
Ni:Cr: Cu:Zn 1:3:5:7	- All heavy metals (HM) occurred in clinker. - $Y_{Ni} = 1.4188X_{Ni} + 39.34$ (4.6) - $Y_{Cr} = 1.3676X_{Cr} + 78.42$ (4.3) - $Y_{Cu} = 1.0275X_{Cu} + 130.94$ (4.9) - $Y_{Zn} = 1.007X_{Zn} + 229.56$ (4.12) - WET, conc. HM in CL & Mortar were not over standard.	- HM↑ (0.05-1.0%), FCaO↓ decreased slightly (0.72 reduce to 0.62<1.5% OK.) - but 2.0%wt.HM, FCaO↑ 1.92% because Cu contained in KF about 6358 ppm and in CL about 6435 ppm. - FCaO, SCCC std. <1.5%.	- 2%wt.HM Light Green, because Cr contained 5000 ppm affected to color of clinker.	- 2.0%wt.HM, C_2S↑, C_3S↓ found that C_2S> C_3S > C_4AF (XRD).	- At 2.0%wt.HM found that HM occurred in C_3S-Cr, Cu, Zn C_2S-Cr, Cu, Ni, Zn C_4AF-Cr, Zn - All HMs were incorporated into clinker phase during the burning process.	- 0.05-0.3%wt. HM , strength ↑ > 400 kg/cm^2 (439.31 and 417.52 kg/cm^2, respectively). - 0.5-2.0%%wt. HM , strength ↓ < 400 kg/cm^2. - 0.05%wt.HM was given highest compressive strength at 1 d & 28 d = 138.98 & 439.731 kg/cm^2, respectively. - 2.0%wt.HM, strength↓ was dropped at 28 d = 331.02 kg/cm^2,	Combination of Ni:Cr:Cu:Zn = 1:3:5:7 < 3000 ppm

APPENDIX E

Table E.1: Free lime in the clinker control and clinker samples.

Sample	Free CaO (%)
Clinker from manufacturing	0.660
Control clinker	0.780
Cr: 1000 ppm	1.260
Cr: 5000 ppm	1.120
Cr: 10000 ppm	2.820
Cr: 20000 ppm	2.220
Cu: 1000 ppm	0.780
Cu: 5000 ppm	1.160
Cu: 10000 ppm	11.460
Cu: 20000 ppm	12.700
Ni: 1000 ppm	0.500
Ni: 5000 ppm	0.770
Ni: 10000 ppm	0.600
Ni: 20000 ppm	1.000
Zn: 1000 ppm	0.890
Zn: 5000 ppm	0.780
Zn: 10000 ppm	0.830
Zn: 20000 ppm	0.830
Combination I = Ni:Cr:Cu:Zn=1:1:1:1=500 ppm (125:125:125:125)	0.660
Combination I = Ni:Cr:Cu:Zn=1:1:1:1=3000 ppm (750:750:750:750)	0.880
Combination I = Ni:Cr:Cu:Zn=1:1:1:1=5000 ppm (1250:1250:1250:1250)	0.720
Combination I = Ni:Cr:Cu:Zn=1:1:1:1=10000 ppm (2500:2500:2500:2500)	0.670
Combination I = Ni:Cr:Cu:Zn=1:1:1:1=20000 ppm (5000:5000:5000:5000)	1.210
Combination II = Ni:Cr:Cu:Zn=1:3:5:7=500 ppm (31.25/93.75/156.25/218.75)	0.720
Combination II = Ni:Cr:Cu:Zn=1:3:5:7=3000 ppm (187.50/562.50/937.50/1312.50)	0.660
Combination II = Ni:Cr:Cu:Zn=1:3:5:7=5000 ppm (312.5/937.5/1562.5/2187.50)	0.610
Combination II = Ni:Cr:Cu:Zn=1:3:5:7=10000 ppm (625/1875/2500/4375)	0.620
Combination II = Ni:Cr:Cu:Zn=1:3:5:7=20000 ppm (1250/3750/6250/8750)	1.920

Table E.2: The results of chemical analysis by XRF.

Description	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	P_2O_5	Mn_2O_3	Cl	LOI	FCaO	SUM	IR	LSF	SM	AM	S/A	Na2Oeq	C_3S	C_2S	C_3A	C_4AF
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%					%	%	%	%	%
Kiln Feed	15.610	3.610	2.760	44.850	1.120	0.440	0.130	0.690	0.094	0.080	0.048	0.0220	30.560	-	100.01	-	89.9988	2.4505	1.3080	4.9400	0.4200	-	-	-	-
Clinker of SCCC	22.330	5.270	3.620	65.570	1.470	0.540	0.160	0.780	0.203	0.083	0.058	0.0089	0.000	0.660	100.09	0.0000	92.2100	2.5100	1.4600		0.5200	54.3600	23.0200	7.8500	11.0100
Control clinker	22.280	7.030	3.360	65.140	1.270	0.430	0.190	1.020	0.200	0.090	0.072	0.0051	0.000	0.780	101.09	0.0000	89.3900	2.1400	2.0900		0.4800	40.8800	33.0400	12.9500	10.2200
Cr:1000ppm	22.410	6.040	3.280	65.410	1.260	0.530	0.190	1.100	0.216	0.091	0.072	0.0069	0.000	1.260	100.61	0.0000	90.8400	2.4100	1.8400		0.5400	47.5700	28.3600	10.4500	9.9800
Cr:5000ppm	21.330	5.990	3.210	65.030	1.290	0.530	0.160	1.140	0.191	0.088	0.074	0.0061	0.000	1.120	99.04	0.0000	94.4200	2.3200	1.8600		0.5100	54.5700	19.9700	10.4500	9.7800
Cr:10000ppm	20.460	6.450	3.030	64.560	1.320	0.490	0.160	0.920	0.192	0.086	0.079	0.0049	0.000	2.820	97.75	0.0000	96.5300	2.1600	2.1300		0.4800	57.0100	15.6600	11.9800	9.2100
Cr:20000ppm	19.000	6.410	2.800	63.020	1.270	0.620	0.160	1.050	0.193	0.085	0.085	0.0041	0.000	2.220	94.70	0.0000	100.7100	2.0600	2.2900		0.5600	62.1000	7.6200	12.2600	8.5100
Cu:1000ppm	22.680	5.990	3.300	65.610	1.250	0.440	0.180	1.030	0.206	0.092	0.071	0.0063	0.000	0.780	100.86	0.0000	90.2300	2.4400	1.8100		0.4700	46.8400	29.6900	10.2700	10.0500
Cu:5000ppm	22.340	6.310	3.300	65.180	1.250	0.450	0.180	1.040	0.209	0.091	0.071	0.0075	0.000	1.160	100.43	0.0000	90.3600	2.3200	1.9200		0.4800	45.4900	29.7300	11.1600	10.0300
Cu:10000ppm	21.310	6.580	3.400	64.940	1.190	0.350	0.170	0.850	0.204	0.086	0.073	0.0037	0.000	11.460	99.16	0.0000	93.2500	2.1300	1.9400		0.4000	50.9200	22.6800	11.6900	10.3500
Cu:20000ppm	21.290	6.130	3.200	64.040	1.070	0.490	0.200	1.120	0.181	0.087	0.071	0.0046	0.000	12.700	97.88	0.0000	92.9000	2.2800	1.9200		0.5200	49.9200	23.3900	10.8400	9.7400
Ni:1000ppm	21.930	6.960	3.460	65.140	1.260	0.390	0.170	1.010	0.238	0.089	0.073	0.0049	0.000	0.500	100.72	0.0000	90.6600	2.1000	2.0100		0.4300	43.9800	29.6800	12.5800	10.5300
Ni:5000ppm	21.720	6.480	3.370	64.770	1.040	0.400	0.180	0.990	0.238	0.089	0.074	0.0045	0.000	0.770	99.36	0.0000	91.6700	2.2000	1.9200		0.4400	47.4000	26.5000	11.4700	10.2600
Ni:10000ppm	20.680	6.830	3.500	64.000	0.860	0.450	0.170	0.980	0.208	0.086	0.075	0.0051	0.000	0.600	97.84	0.0000	93.7800	2.0000	1.9500		0.4700	49.6500	21.8300	12.1900	10.6400
Ni:20000ppm	18.150	7.660	3.860	62.310	0.760	0.300	0.150	0.860	0.310	0.083	0.088	0.0054	0.370	1.000	94.91	0.0000	99.9000	1.5800	1.9900		0.3500	56.2700	9.5900	13.7900	11.7300
Zn:1000ppm	21.950	5.770	3.310	65.840	1.240	0.280	0.180	0.830	0.232	0.093	0.068	0.0056	0.350	0.890	100.15	0.0000	93.5000	2.4200	1.7400		0.3600	55.3500	21.1800	9.6900	10.0600
Zn:5000ppm	21.560	5.840	3.300	65.320	1.210	0.370	0.250	0.970	0.255	0.092	0.070	0.0056	0.410	0.780	99.65	0.0000	94.1200	2.3600	1.7700		0.5000	55.3700	20.0400	9.8900	10.0400
Zn:10000ppm	20.580	6.160	3.380	64.470	1.130	0.390	0.330	0.960	0.273	0.089	0.076	0.0052	0.310	0.830	98.15	0.0000	96.1100	2.1600	1.8200		0.5800	57.1400	15.8800	10.6100	10.2700
Zn:20000ppm	20.170	6.770	3.260	63.640	1.100	0.380	0.470	0.960	0.290	0.088	0.072	0.0073	0.310	0.830	97.52	0.0000	95.5900	2.0100	2.0800		0.7200	52.9400	17.8800	12.4200	9.9200
Com I :500ppm	21.330	6.600	3.530	65.190	1.270	0.370	0.120	1.080	0.259	0.090	0.073	0.0000	0.410	0.660	100.32	0.0000	92.3300	2.1100	1.8700		0.3600	50.8800	22.7500	11.5200	10.7300
Com I :3000ppm	21.900	6.490	3.370	64.930	1.250	0.420	0.210	1.080	0.229	0.088	0.070	0.0045	0.000	0.880	100.04	0.0000	91.2200	2.2200	1.9300		0.4900	46.3500	27.8300	11.5000	10.2500
Com I :5000ppm	21.510	7.120	3.410	64.640	1.230	0.370	0.210	1.070	0.220	0.088	0.071	0.0061	0.000	0.720	99.95	0.0000	91.2600	2.0400	2.0900		0.4600	43.9300	28.5100	13.1100	10.3800
Com I :10000ppm	21.270	6.930	3.240	64.150	1.100	0.380	0.240	1.100	0.209	0.087	0.073	0.0065	0.000	0.670	98.79	0.0000	91.8800	2.0900	2.1400		0.4900	45.2400	26.8400	12.8700	9.8700
Com I :20000ppm	19.680	7.500	3.240	62.800	0.930	0.460	0.270	1.240	0.250	0.084	0.078	0.0078	0.000	1.210	96.54	0.0000	95.0500	1.8300	2.3100		0.5700	47.5300	20.5700	14.3900	9.8700
Com II :500ppm	21.280	6.920	3.520	65.030	1.280	0.380	0.120	1.100	0.290	0.089	0.073	0.0000	0.390	0.720	100.47	0.0000	91.7700	2.0400	1.9600		0.3600	48.4100	24.4800	12.3700	10.7100
Com II :3000ppm	22.390	6.240	3.280	64.940	1.230	0.610	0.220	1.030	0.202	0.089	0.071	0.0066	0.000	0.660	100.31	0.0000	89.9700	2.3500	1.9000		0.6200	44.6900	30.4800	10.9800	9.9800
Com II :5000ppm	21.890	6.640	3.290	64.740	1.210	0.560	0.230	1.030	0.186	0.088	0.072	0.0058	0.000	0.610	99.94	0.0000	90.8300	2.2000	2.0200		0.6000	44.9300	28.8800	12.0100	10.0200
Com II :10000ppm	21.710	6.470	3.240	64.280	1.140	0.490	0.270	1.000	0.214	0.089	0.071	0.0061	0.000	0.620	98.98	0.0000	91.1300	2.2400	2.0000		0.6000	45.7200	27.7600	11.6600	9.8600
Com II :20000ppm	20.710	6.840	3.190	63.320	1.000	0.560	0.340	1.040	0.191	0.087	0.071	0.0061	0.000	1.920	97.36	0.0000	92.9300	2.0700	2.1500		0.7100	46.9000	24.0000	12.7300	9.7000

Remark: 1. Com I : Combination I = Ni:Cr:Cu:Zn=1:1:1:1
2. Com II : Combination II = Ni:Cr:Cu:Zn=1:3:5:7

Lime saturation factor (LSF) = $\% CaO / (2.8x\%SiO_2 + 1.2x\%Al_2O_3 + 0.65x\%Fe_2O_3)$
Silica modulus (SM) = $\%SiO_2 / (\%Al_2O_3 + \%Fe_2O_3)$
Alumina modulus (AM) = $\% Al_2O_3 / \%Fe_2O_3$

Table E.3: The results of chemical analysis by XRD.

Description	C_3S	C_2S	C_3A-cub	C_3A-ortho	C_4AF	MgO	K2SO4	FCaO
	%	%	%	%	%	%	%	%
Kiln Feed	-	-	-	-	-	-	-	-
Clinker of SCCC	58.400	23.500	2.200	0.200	14.600	-	0.800	0.400
Control clinker	43.100	36.000	4.900	1.400	13.400	-	0.600	0.500
Cr:1000ppm	50.300	29.000	4.100	1.000	13.600	0.800	0.900	0.400
Cr:5000ppm	37.500	41.800	2.500	1.400	15.400	0.200	1.000	0.200
Cr:10000ppm	22.100	54.800	2.400	0.900	17.100	0.500	0.800	0.600
Cr:20000ppm	17.300	59.100	1.600	1.600	19.100	0.200	1.900	0.300
Cu:1000ppm	52.700	27.000	3.600	1.700	13.800	0.300	0.500	0.400
Cu:5000ppm	48.500	29.500	3.300	1.700	15.200	0.200	0.700	0.800
Cu:10000ppm	8.600	58.100	3.900	1.600	18.900	0.600	1.500	6.600
Cu:20000ppm	12.600	54.500	3.600	1.900	19.000	0.600	2.400	5.400
Ni:1000ppm	45.300	32.600	4.800	0.100	15.600	0.300	0.800	0.500
Ni:5000ppm	44.300	34.000	4.600	0.700	14.300	0.800	0.800	0.600
Ni:10000ppm	47.100	27.500	5.300	0.800	17.100	0.700	1.200	0.400
Ni:20000ppm	38.700	32.100	6.900	1.200	16.900	1.600	1.800	0.900
Zn:1000ppm	53.000	28.000	3.300	1.400	13.600	-	0.600	0.300
Zn:5000ppm	47.900	32.700	2.800	0.900	14.400	0.300	0.400	0.900
Zn:10000ppm	48.300	27.200	2.900	2.300	17.000	-	1.300	0.600
Zn:20000ppm	43.000	34.000	3.900	-	16.300	-	1.800	0.200
Combination I :500ppm	45.900	30.900	5.000	2.200	14.800	0.400	0.600	0.200
Combination I :3000ppm	46.500	32.600	3.600	1.300	14.500	0.400	0.600	0.400
Combination I :5000ppm	41.800	35.700	4.700	0.300	15.300	0.900	0.800	0.600
Combination I :10000ppm	37.600	39.900	3.800	0.600	15.600	1.500	0.500	0.600
Combination I :20000ppm	29.400	46.800	2.700	-	17.300	1.700	1.700	0.700
Combination II :500ppm	43.300	33.200	5.400	2.100	14.800	0.200	0.600	0.500
Combination II :3000ppm	66.000	14.400	3.500	-	14.700	-	-	1.500
Combination II :5000ppm	50.700	27.700	4.900	0.300	15.100	0.300	0.800	0.300
Combination II :10000ppm	45.100	33.400	4.200	0.900	14.500	0.700	0.600	0.500
Combination II :20000ppm	33.700	44.000	2.800	1.600	14.900	0.900	1.000	1.100

Table E.4: The results of compressive strength.

Description	1 Day						3 Days						7 Days						28 Days						
	Force (KN)						Force (KN)						Force (KN)						Force (KN)						Blaine
	1	2	3	AVG	SD	Kg/cm^2	1	2	3	AVG	SD	Kg/cm^2	1	2	3	AVG	SD	Kg/cm^2	1	2	3	AVG	SD	Kg/cm^2	cm^2/g
Clinker of SCCC	29.00	28.30	29.00	28.77	0.40	117.46	58.40	58.40	54.20	57.00	2.42	232.83	80.10	77.40	79.20	78.90	1.37	322.31	100.40	99.70	101.60	100.56	0.96	410.84	3486
Control clinker	31.90	31.90	31.80	31.87	0.06	130.13	58.70	54.10	56.50	56.43	2.30	230.51	75.70	70.80	75.20	73.90	2.70	301.88	102.90	104.20	100.20	102.43	2.04	418.47	3465
Cr:1000ppm	26.10	27.60	28.10	27.26	1.04	111.33	51.40	53.80	50.10	51.76	1.88	211.44	68.30	71.70	69.10	69.70	1.78	284.72	88.20	96.80	84.10	89.70	6.48	366.44	3418
Cr:5000ppm	29.82	31.10	31.33	30.75	0.81	125.37	47.85	47.96	47.80	47.87	0.08	195.20	60.10	59.20	60.34	59.88	0.60	244.17	83.40	83.60	83.41	83.47	0.11	340.35	3481
Cr:10000ppm	16.15	15.65	15.72	15.84	0.27	64.59	30.25	29.67	29.18	29.70	0.54	121.12	38.10	36.90	36.45	37.15	0.85	151.46	56.10	55.90	56.33	56.11	0.22	228.78	3459
Cr:20000ppm	4.60	4.60	4.10	4.43	0.29	18.03	16.80	15.80	19.30	17.30	1.80	70.60	33.30	34.30	35.90	34.50	1.31	140.88	47.90	54.00	56.10	52.66	4.26	215.11	3465
Cu:1000ppm	38.00	38.10	39.00	38.36	0.55	156.68	63.60	62.30	61.40	62.43	1.11	255.03	70.00	78.50	72.50	73.66	4.37	300.92	100.90	95.00	98.20	98.03	2.95	400.48	3584
Cu:5000ppm	21.20	18.50	23.60	21.10	2.55	86.13	53.60	50.90	49.80	51.43	1.96	210.08	65.60	65.60	62.40	64.53	1.85	263.61	80.60	78.30	82.90	80.60	2.30	329.25	3585
Cu:10000ppm	cement was not set			-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3594
Cu:20000ppm	cement was not set			-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3490
Ni:1000ppm	28.20	28.50	28.60	28.43	0.21	116.10	52.30	52.80	53.80	52.90	0.76	216.34	68.40	70.90	72.00	70.43	1.84	287.71	100.20	95.80	98.00	98.00	2.20	400.35	3481
Ni:5000ppm	33.70	34.80	33.40	33.96	0.74	138.70	64.10	64.50	63.80	64.13	0.35	261.97	73.10	79.90	78.90	77.30	3.67	315.73	103.90	104.80	98.00	102.23	3.69	417.65	3585
Ni:10000ppm	30.20	31.00	32.70	31.30	1.28	127.81	62.70	63.00	61.60	62.43	0.74	255.30	94.70	89.40	84.40	89.50	5.15	365.60	102.00	103.20	100.10	101.76	1.56	415.74	3531
Ni:20000ppm	29.50	30.20	28.20	29.30	1.01	119.64	55.90	61.90	61.40	59.73	3.33	243.99	73.90	66.80	64.80	68.50	4.78	279.77	102.90	95.00	98.90	98.93	3.95	404.16	3433
Zn:1000ppm	35.80	36.50	39.20	37.17	1.80	151.79	64.40	64.90	62.80	64.03	1.10	261.56	76.50	80.10	74.40	77.00	2.88	314.54	90.80	94.80	94.80	93.46	2.31	401.12	3574
Zn:5000ppm	26.20	27.00	26.20	26.46	0.46	108.06	64.70	63.50	64.50	64.23	0.64	262.38	82.70	79.80	83.20	81.90	1.84	334.57	94.60	93.20	99.00	95.60	3.03	400.28	3553
Zn:10000ppm	33.80	34.20	34.60	34.20	0.40	139.66	64.80	62.40	63.90	63.70	1.21	260.20	78.00	83.20	81.60	80.93	2.66	330.58	105.30	101.60	104.90	103.93	2.03	424.59	3582
Zn:20000ppm	17.10	16.40	17.30	16.93	0.47	69.10	43.20	41.80	46.20	43.75	2.25	178.61	53.30	50.70	54.60	52.86	1.99	215.87	80.90	85.60	79.30	81.93	3.27	334.67	3441
Com I :500ppm	33.17	33.16	33.15	33.16	0.01	135.19	59.14	59.16	59.18	59.16	0.02	241.24	84.10	83.85	83.90	83.95	0.13	342.31	102.40	102.55	102.43	102.46	0.08	417.78	3475
Com I :3000ppm	31.30	30.50	29.80	30.53	0.75	124.68	50.40	49.00	47.30	48.90	1.55	199.72	73.75	73.60	73.48	73.61	0.14	300.17	98.65	97.85	98.40	98.30	0.41	400.82	3442
Com I :5000ppm	25.70	27.30	26.50	26.50	0.80	108.19	44.60	42.80	46.60	44.66	1.90	182.43	61.65	62.10	61.83	61.86	0.23	252.27	89.80	88.95	89.24	89.33	0.43	364.28	3418
Com I :10000ppm	26.06	25.30	24.40	25.23	0.83	103.02	50.30	45.40	46.80	49.50	2.52	194.00	64.20	63.70	63.10	63.66	0.55	260.06	96.30	93.60	92.50	94.13	1.96	384.55	3424
Com I :20000ppm	16.60	19.10	20.90	18.86	2.16	77.00	39.40	43.40	41.10	41.30	2.01	168.69	60.40	62.00	53.80	58.73	4.35	239.90	81.70	87.10	85.00	84.60	2.72	345.60	3458
Com II :500ppm	37.20	32.10	32.80	34.03	2.76	138.98	63.00	61.00	60.60	61.53	1.29	251.35	88.50	82.90	82.40	84.60	3.39	345.60	109.40	99.40	113.80	107.53	7.38	439.31	3479
Com II :3000ppm	27.70	30.20	27.60	28.50	1.47	116.37	53.80	59.50	52.00	59.45	3.92	222.33	76.60	74.30	75.40	75.43	1.15	308.15	102.10	104.30	100.20	102.20	2.05	417.52	3457
Com II :5000ppm	27.90	28.10	28.90	28.23	0.53	115.28	48.40	48.40	46.30	47.70	1.21	194.82	67.00	65.30	66.10	66.33	0.85	270.96	86.70	91.70	97.90	92.10	5.61	376.25	3455
Com II :10000ppm	10.80	10.40	10.60	10.60	0.20	43.23	22.80	23.20	25.50	23.80	1.46	97.30	41.20	42.10	41.00	43.43	0.59	169.21	64.80	60.70	59.60	61.70	2.74	252.03	3408
Com II :20000ppm	21.70	21.30	22.30	21.96	0.50	89.67	44.60	45.80	42.50	44.30	1.67	180.93	56.20	58.70	62.00	58.96	2.91	240.86	81.60	81.20	80.30	81.03	0.67	331.02	3412

Remark: ASTM: Strength: $\text{kg/cm}^2 = \dfrac{\text{KNx1000}}{\text{25x9.81}}$

$\text{MPa} = \text{N/mm}^2 = \dfrac{\text{Psi}}{145} = 0.1\ \text{Kg/cm}^2$

If area of mortar is between 24.62 – 25.37 cm^2 (over 1.5%), Strength: $\text{kg/cm}^2 = \dfrac{\text{KNx1000}}{\text{Areax9.81}}$

Table E.5: The results of total concentration (ppm) of heavy metals in kiln feed.

Description	Cr (ppm)					Cu (ppm)					Ni (ppm)					Zn (ppm)				
	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD
Control	50.56	42.68	43.35	45.53	4.37	75.25	70.68	72.65	72.86	2.29	27.45	24.13	25.61	25.73	1.66	162.53	156.23	153.53	157.43	4.62
Cr:1000ppm	1263	1154	850	1089	214.04															
Cr:5000ppm	4920	5120	4945	4995	108.97															
Cr:10000ppm	10187	9864	10120	10057	170.47															
Cr:20000ppm	20185	20450	20109	20248	179.02															
Cu:1000ppm						1120	950	891	987	118.90										
Cu:5000ppm						5098	4920	4937	4985	98.23										
Cu:10000ppm						10130	9945	9784	9953	173.14										
Cu:20000ppm						20078	19825	19689	19864	197.41										
Ni:1000ppm											1257	1105	1013	1125	123.22					
Ni:5000ppm											5321	5205	5122	5216	99.95					
Ni:10000ppm											10254	10198	10241	10231	29.31					
Ni:20000ppm											19950	19820	19915	19895	67.27					
Zn:1000ppm																1298	1250	1307	1285	30.64
Zn:5000ppm																5165	5152	5127	5148	19.31
Zn:10000ppm																10162	10185	10166	10171	12.29
Zn:20000ppm																19985	19946	19925	19952	30.45
Com I :500ppm	156	142	137	145	9.85	196	175	196	189	12.12	162	152	109	141	28.16	272	254	269	265	9.64
Com I :3000ppm	752	815	740	769	40.29	765	742	638	715	67.67	823	775	745	781	39.34	873	912	882	889	20.42
Com I :5000ppm	1196	1183	1146	1175	25.94	1312	1210	1141	1221	86.03	1250	1342	1245	1279	54.62	1513	1389	1502	1468	68.64
Com I :10000ppm	2568	2468	2449	2495	63.93	2475	2654	2554	2561	89.71	2684	2586	2524	2598	80.67	2753	2641	2631	2675	67.73
Com I :20000ppm	5126	5105	4943	5058	100.14	5087	4895	5093	5025	112.62	5424	5305	5207	5312	108.67	5358	5279	5125	5254	118.49
Com II :500ppm	156	110	94	120	32.19	257	231	166	218	46.87	53	35	33.56	40.52	10.83	386	310	249	315	68.64
Com II :3000ppm	692	569	494	585	99.96	1135	905	1002	1014	115.47	195	276	159	210	59.92	1498	1510	1384	1464	69.54
Com II :5000ppm	959	985	1092	1012	70.49	1625	1525	1524	1558	58.03	396	332	256	328	70.09	2270	2321	2267	2285	30.35
Com II :10000ppm	2106	1869	1980	1985	118.58	2484	2583	2475	2514	59.92	758	622	654	678	71.11	4278	4512	4518	4436	136.86
Com II :20000ppm	4021	3875	3930	3942	73.74	6302	6423	6349	6358	61.00	1389	1278	1293	1320	60.22	8764	8913	8795	8824	78.62

Remark:
1. Com I : Combination I = Ni:Cr:Cu:Zn=1:1:1:1
2. Com II : Combination II = Ni:Cr:Cu:Zn=1:3:5:7

Table E.6: The results of total concentration (ppm) of heavy metals in clinker.

Description	Cr (ppm)					Cu (ppm)					Ni (ppm)					Zn (ppm)				
	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD
Control	95.54	70.23	69.49	78.42	14.83	145.62	115.62	131.58	130.94	15.01	30.26	49.56	38.2	39.34	9.70	250.24	228.1	210.34	229.56	95.54
Cr:1000ppm	1520	1730	1784	1678	139.47															
Cr:5000ppm	7568	7465	7311	7448	129.34															
Cr:10000ppm	14953	15115	15145	15071	103.29															
Cr:20000ppm	28534	28247	28716	28499	236.45															
Cu:1000ppm						2050	1925	1860	1945	96.57										
Cu:5000ppm						7750	7586	7713	7683	86.02										
Cu:10000ppm						12130	12256	12052	12146	102.94										
Cu:20000ppm						29185	29290	29350	29275	83.52										
Ni:1000ppm											2018	1950	1924	1964	48.54					
Ni:5000ppm											10502	10652	10604	10586	76.60					
Ni:10000ppm											15756	15784	15845	15795	45.51					
Ni:20000ppm											29658	29550	29526	29578	70.31					
Zn:1000ppm																1562	1445	1358	1455	102.37
Zn:5000ppm																5825	5663	5726	5738	81.66
Zn:10000ppm																10189	10295	10425	10303	118.20
Zn:20000ppm																21007	21143	21123	21091	73.43
Com I :500ppm	319	235	268	274	42.32	310	243	251	268	36.59	268	252	176	232	49.15	310	284	303	299	319
Com I :3000ppm	1375	1204	1195	1258	101.42	724	812	786	774	45.21	1112	1105	1158	1125	28.79	893	910	945	916	1375
Com I :5000ppm	1918	1924	1993	1945	41.68	1239	1325	1198	1254	64.82	1877	1825	1923	1875	49.03	1450	1498	1447	1465	1918
Com I :10000ppm	3176	3285	3109	3210	88.83	2735	2679	2824	2746	73.12	3008	3008	2912	2976	55.43	2695	2752	2677	2708	3176
Com I :20000ppm	7498	7612	7609	7573	64.97	5274	5245	5321	5280	38.35	9148	9162	9215	9175	35.34	5607	5648	5608	5621	7498
Com II :500ppm	207	231	327	255	63.50	280	284	312	292	17.44	74.21	68.45	84.23	75.63	7.99	373	410	387	390	207
Com II :3000ppm	982	1085	987	1018	58.08	1295	1212	1297	1268	48.51	412	398	435	415	18.68	1486	1523	1506	1505	982
Com II :5000ppm	1797	1705	1826	1776	63.17	1685	1723	1677	1695	24.58	576	565	596	579	15.72	2285	2395	2289	2323	1797
Com II :10000ppm	2812	3056	2895	2921	124.06	2957	2895	3010	2954	57.56	968	1012	1089	1023	61.25	4501	4512	4595	4536	2812
Com II :20000ppm	4905	5021	4885	4937	73.43	6389	6485	6431	6435	48.12	1649	1798	1725	1724	74.51	9178	9086	9114	9126	4905

Remark:
1. Com I : Combination I = Ni:Cr:Cu:Zn=1:1:1:1
2. Com II : Combination II = Ni:Cr:Cu:Zn=1:3:5:7

Table E.7: The results of total concentration (ppm) of heavy metals in cement mortar.

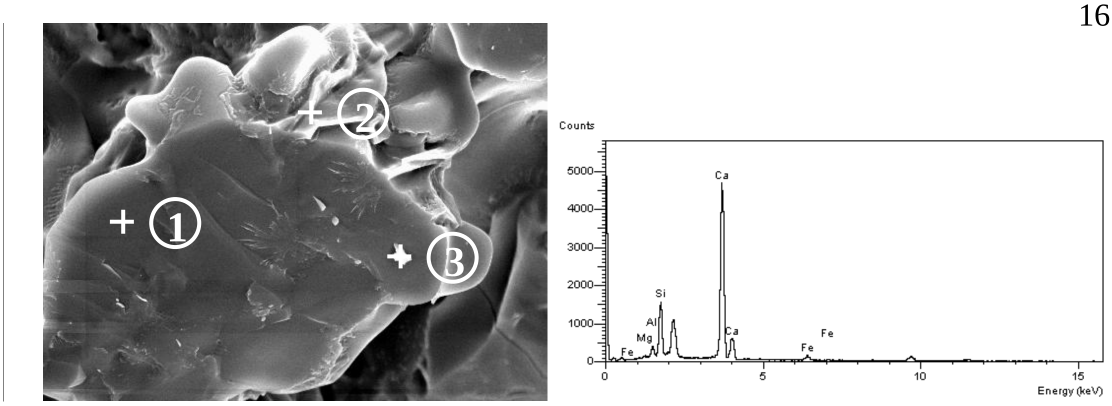
Description	Cr (ppm)					Cu (ppm)					Ni (ppm)					Zn (ppm)				
	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD	1	2	3	AVG	SD
Control	21.65	17.87	20.03	19.85	1.90	35.54	25.67	26.09	29.1	5.58	15.87	6.31	8.87	10.35	4.95	57.98	42.69	37.06	45.91	10.83
Cr:1000ppm	430	497	459	462	33.60															
Cr:5000ppm	2015	1995	2035	2015	20.00															
Cr:10000ppm	4082	4112	4085	4093	16.52															
Cr:20000ppm	8347	8385	8321	8351	32.19															
Cu:1000ppm						705	685	686	692	11.27										
Cu:5000ppm						2778	2810	2785	2791	16.82										
Cu:10000ppm						4475	4387	4344	4402	66.78										
Cu:20000ppm						10491	10486	10376	10451	65.00										
Ni:1000ppm											752	684	670	702	43.86					
Ni:5000ppm											3533	3611	3512	3552	52.16					
Ni:10000ppm											4956	4950	4863	4923	52.05					
Ni:20000ppm											9492	9597	9486	9525	62.43					
Zn:1000ppm																502	452	375	443	63.98
Zn:5000ppm																1782	1785	1812	1793	16.52
Zn:10000ppm																2952	2986	2885	2941	51.39
Zn:20000ppm																6184	6164	6258	6202	49.52
Com I :500ppm	95.87	103	87.12	95.33	7.95	63.25	95.21	85.23	81.23	16.35	81.48	59.23	94.25	78.32	17.72	79.96	80.12	95.34	85.14	8.83
Com I :3000ppm	394	426	374	398	26.23	421	465	425	437	24.33	412	369	344	375	34.39	456	423	408	429	24.56
Com I :5000ppm	576	625	584	595	26.29	401	485	425	437	43.27	624	562	560	582	36.39	482	471	502	485	15.72
Com I :10000ppm	957	956	1012	975	32.05	859	801	896	852	47.89	882	1025	949	952	71.55	787	850	823	820	31.61
Com I :20000ppm	2523	2498	2587	2536	45.90	1612	1586	1635	1611	24.52	2396	2314	2252	2354	72.23	1545	1676	1597	1606	65.96
Com II :500ppm	74.95	71.23	109	85.06	20.82	88.1	118	88.95	98.35	17.02	14.23	18.26	28.23	20.24	7.21	114	129	108	117	10.82
Com II :3000ppm	268	341	285	298	38.20	376	456	395	409	41.80	115	169	145	143	27.06	412	482	432	442	36.06
Com II :5000ppm	608	482	569	553	64.51	540	611	550	567	38.43	313	324	245	294	42.79	737	765	721	741	22.27
Com II :10000ppm	830	879	823	844	30.51	1166	1184	1154	1168	15.10	360	398	298	352	50.48	2552	2397	2485	2478	77.74
Com II :20000ppm	1629	1521	1623	1591	60.70	2055	2016	2103	2058	43.58	497	546	529	524	24.88	2901	2981	2923	2935	41.33

Remark:
1. Com I : Combination I = Ni:Cr:Cu:Zn=1:1:1:1
2. Com II : Combination II = Ni:Cr:Cu:Zn=1:3:5:7

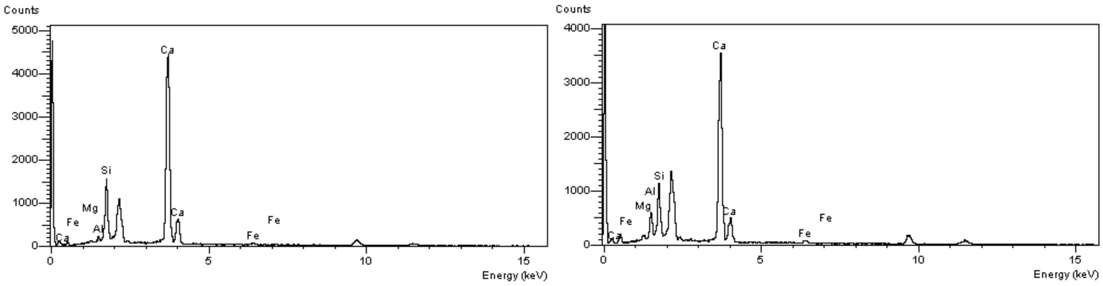
Table E.8: Mass of metal oxides in 1 kg of kiln feed.

Heavy metal	Concentration of HM (ppm)	Concentration, g/ kiln feed 1.0 kg	Molecular weight of metal oxide, g	Atomic weight of heavy metal, g	Mass of metal oxide, g	Heavy metal	Concentration of HM (ppm)	Concentration, g/ kiln feed 1.0 kg	Molecular weight of metal oxide, g	Atomic weight of heavy metal, g	Mass of metal oxide, g
1. Cr (Cr_2O_3)	1,000	1.0000	152	52	2.92	**7. Ni (NiO_2)**	1,000	1.0000	165.4	58.7	2.82
	5,000	5.0000	152	52	14.62		5,000	5.0000	165.4	58.7	14.09
	10,000	10.0000	152	52	29.23		10,000	10.0000	165.4	58.7	28.18
	20,000	20.0000	152	52	58.46		20,000	20.0000	165.4	58.7	56.35
2. Cr in combination ratio Ni:Cr:Cu:Zn = 1:1:1:1						**8. Ni in combination ratio Ni:Cr:Cu:Zn = 1:1:1:1**					
Com I=500ppm	125	0.1250	152	52	0.37	Com I=500ppm	125	0.1250	90.7	58.7	0.19
Com I=3,000ppm	750	0.7500	152	52	2.19	Com I=3,000ppm	750	0.7500	90.7	58.7	1.16
Com I=5,000ppm	1,250	1.2500	152	52	3.65	Com I=5,000ppm	1,250	1.2500	90.7	58.7	1.93
Com I=10,000ppm	2,500	2.5000	152	52	7.31	Com I=10,000ppm	2,500	2.5000	90.7	58.7	3.86
Com I=20,000ppm	5,000	5.0000	152	52	14.62	Com I=20,000ppm	5,000	5.0000	90.7	58.7	7.73
3. Cr in combination ratio Ni:Cr:Cu:Zn = 1:3:5:7						**9. Ni in combination ratio Ni:Cr:Cu:Zn = 1:3:5:7**					
Com II=500ppm	93.75	0.0938	152	52	0.27	Com II=500ppm	31.25	0.0313	90.7	58.7	0.05
Com II=3,000ppm	562.50	0.5625	152	52	1.64	Com II=3,000ppm	187.50	0.1875	90.7	58.7	0.29
Com II=5,000ppm	937.50	0.9375	152	52	2.74	Com II=5,000ppm	312.50	0.3125	90.7	58.7	0.48
Com II=10,000ppm	1,875.00	1.8750	152	52	5.48	Com II=10,000ppm	625.00	0.6250	90.7	58.7	0.97
Com II=20,000ppm	3,750.00	3.7500	152	52	10.96	Com II=20,000ppm	1,250.00	1.2500	90.7	58.7	1.93
4. Zn (ZnO)	1,000	1.0000	81.39	65.39	1.24	**10. Cu (CuO)**	1,000	1.0000	79.55	63.55	1.25
	5,000	5.0000	81.39	65.39	6.22		5,000	5.0000	79.55	63.55	6.26
	10,000	10.0000	81.39	65.39	12.45		10,000	10.0000	79.55	63.55	12.52
	20,000	20.0000	81.39	65.39	24.89		20,000	20.0000	79.55	63.55	25.04
5. Zn in combination ratio Ni:Cr:Cu:Zn = 1:1:1:1						**11. Cu in combination ratio Ni:Cr:Cu:Zn = 1:1:1:1**					
Com I=500ppm	125	0.1250	81.39	65.39	0.16	Com I=500ppm	125	0.1250	79.55	63.55	0.16
Com I=3,000ppm	750	0.7500	81.39	65.39	0.93	Com I=3,000ppm	750	0.7500	79.55	63.55	0.94
Com I=5,000ppm	1,250	1.2500	81.39	65.39	1.56	Com I=5,000ppm	1,250	1.2500	79.55	63.55	1.56
Com I=10,000ppm	2,500	2.5000	81.39	65.39	3.11	Com I=10,000ppm	2,500	2.5000	79.55	63.55	3.13
Com I=20,000ppm	5,000	5.0000	81.39	65.39	6.22	Com I=20,000ppm	5,000	5.0000	79.55	63.55	6.26
6. Zn in combination ratio Ni:Cr:Cu:Zn = 1:3:5:7						**12. Cu in combination ratio Ni:Cr:Cu:Zn = 1:3:5:7**					
Com II=500ppm	218.75	0.2188	81.39	65.39	0.27	Com II=500ppm	156.25	0.1563	79.55	63.55	0.20
Com II=3,000ppm	1,312.50	1.3125	81.39	65.39	1.63	Com II=3,000ppm	937.50	0.9375	79.55	63.55	1.17
Com II=5,000ppm	2,187.50	2.1875	81.39	65.39	2.72	Com II=5,000ppm	1,562.50	1.5625	79.55	63.55	1.96
Com II=10,000ppm	4,375.00	4.3750	81.39	65.39	5.45	Com II=10,000ppm	3,125.00	3.1250	79.55	63.55	3.91
Com II=20,000ppm	8,750.00	8.7500	81.39	65.39	10.89	Com II=20,000ppm	6,250.00	6.2500	79.55	63.55	7.82

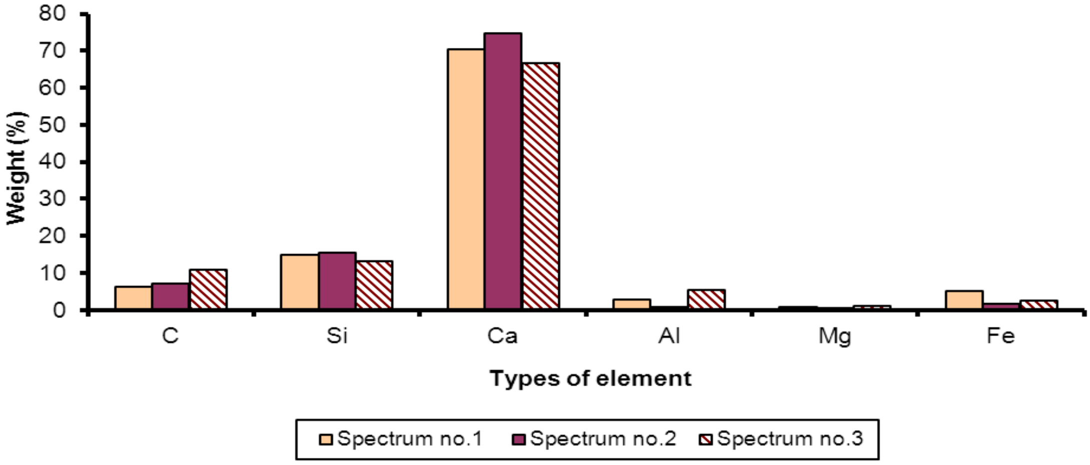
Remark: Concentration of metal oxide (ppm) = [(mass of metal oxide) x (atomic weight of heavy metal / molecular weight) / 1000g of kiln feed] x 10^6



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

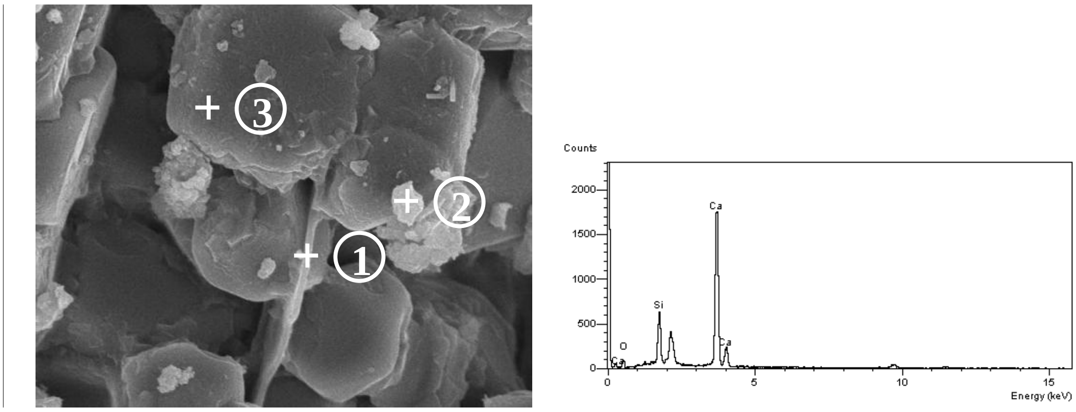


(e) The quantitative results of elements

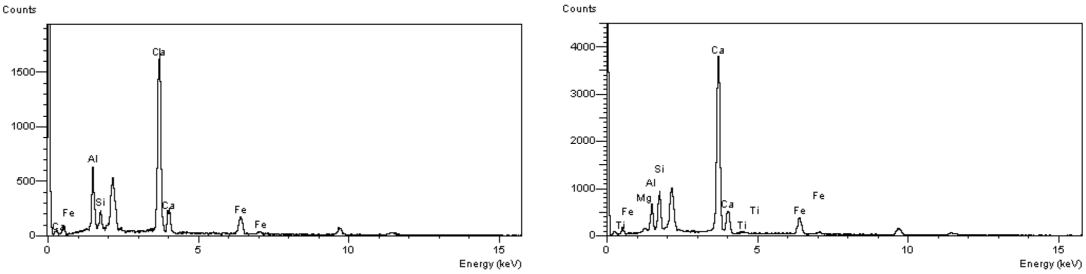
Figure E.1: Analysis of clinker phase of the clinker from manufaturing: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.9: The quantitative result of elements in the clinker phase of the clinker from manufaturing.

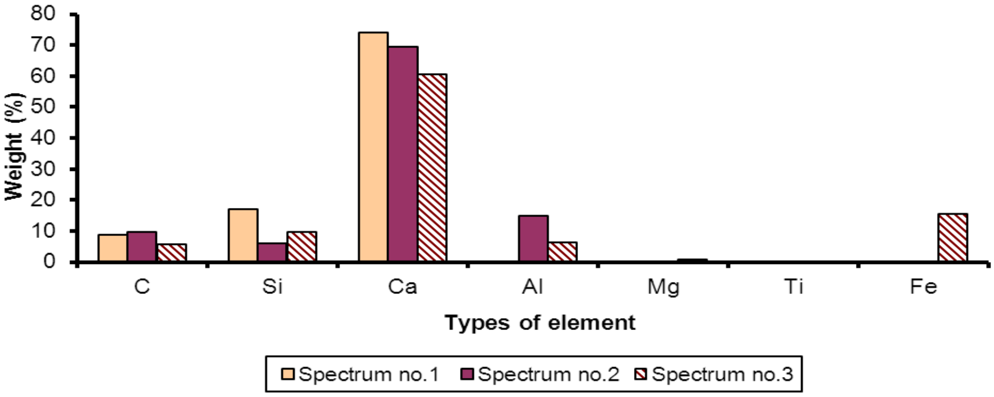
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	6.18	7.16	10.83
Si	14.95	15.34	13.25
Ca	70.51	74.75	66.63
Al	2.67	0.72	5.53
Mg	0.66	0.45	1.12
Fe	5.03	1.58	2.64
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

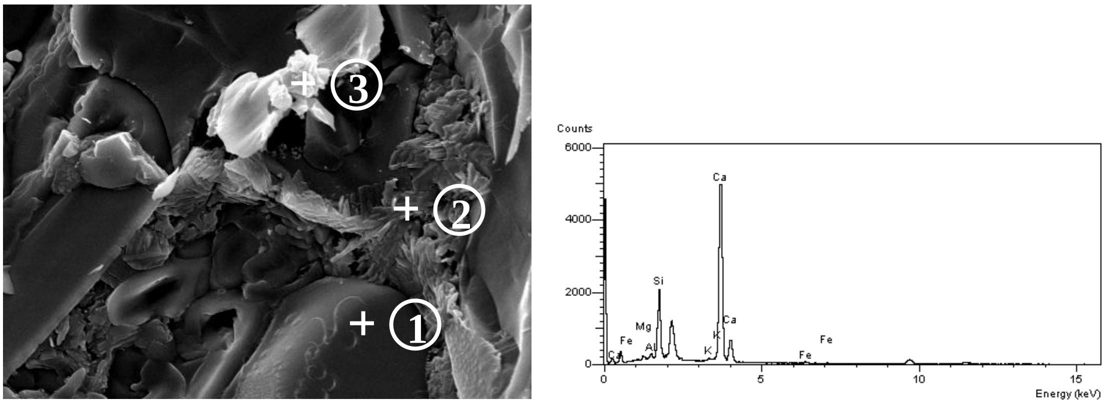


(e) The quantitative results of elements

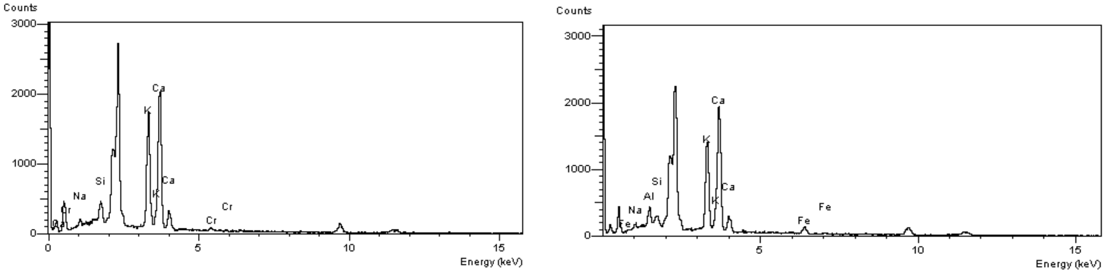
Figure E.2: Analysis of clinker phase of the control clinker: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.10: The quantitative result of elements in the clinker phase of the control clinker.

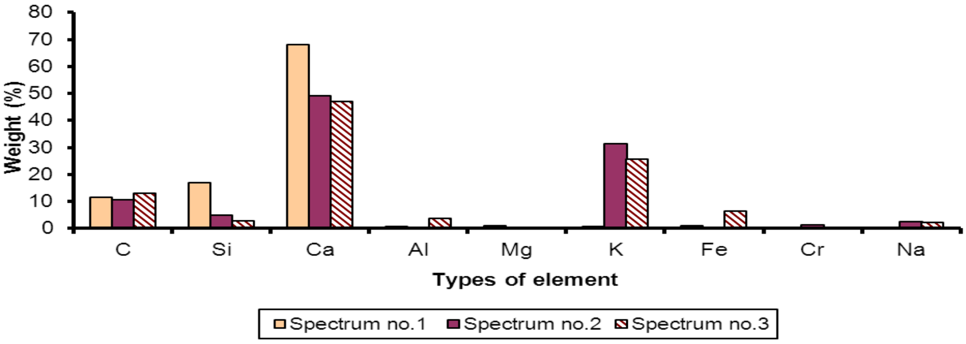
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	8.86	9.57	5.90
Si	17.12	5.95	9.87
Ca	74.02	69.45	60.61
Al	0	15.03	6.48
Mg	0	0	1.00
Ti	0	0	0.65
Fe	0	0	15.49
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

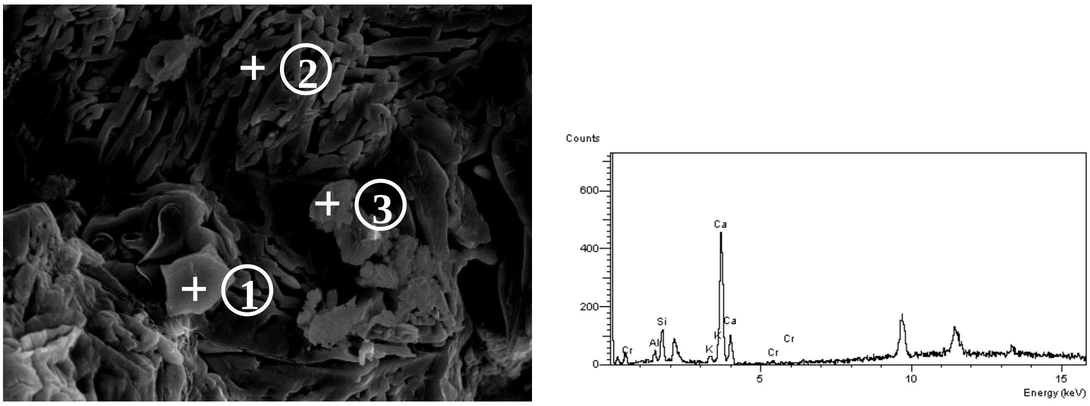


(e) The quantitative results of elements

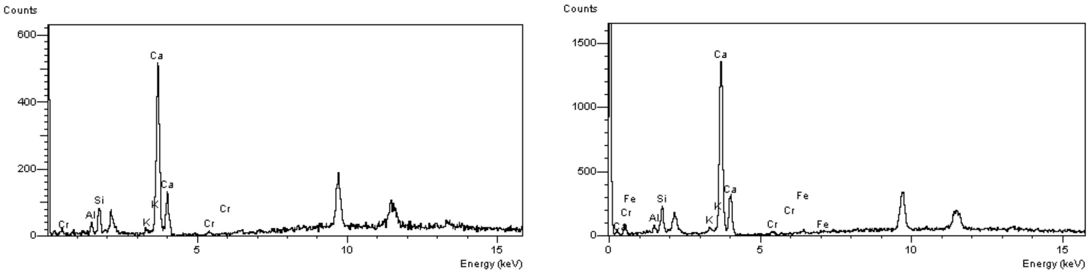
Figure E.3: Analysis of clinker phase with added Cr 1000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.11: The quantitative result of elements in the clinker phase with added Cr 1000 ppm.

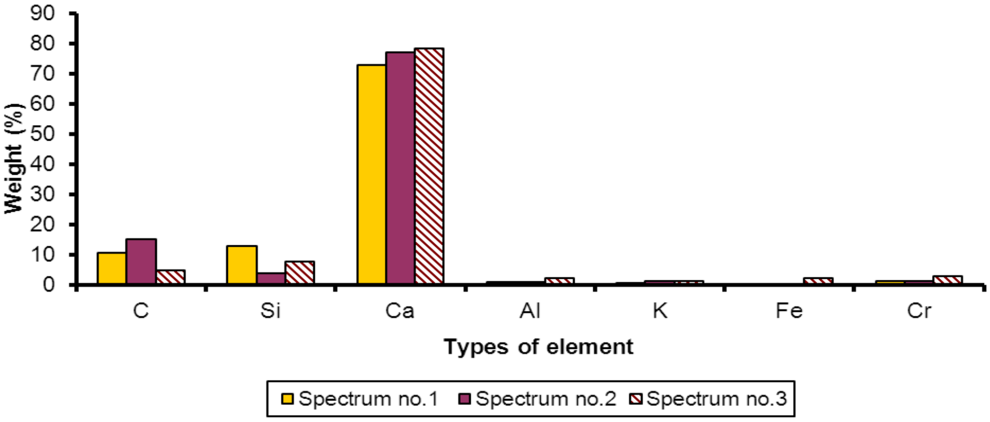
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	11.53	10.55	13.04
Si	16.98	5.02	2.64
Ca	68.00	49.23	46.84
Al	0.69	0	3.69
Mg	1.00	0	0
K	0.64	31.44	25.47
Fe	1.16	0	6.21
Cr	0	1.35	0
Na	0	2.41	2.11
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

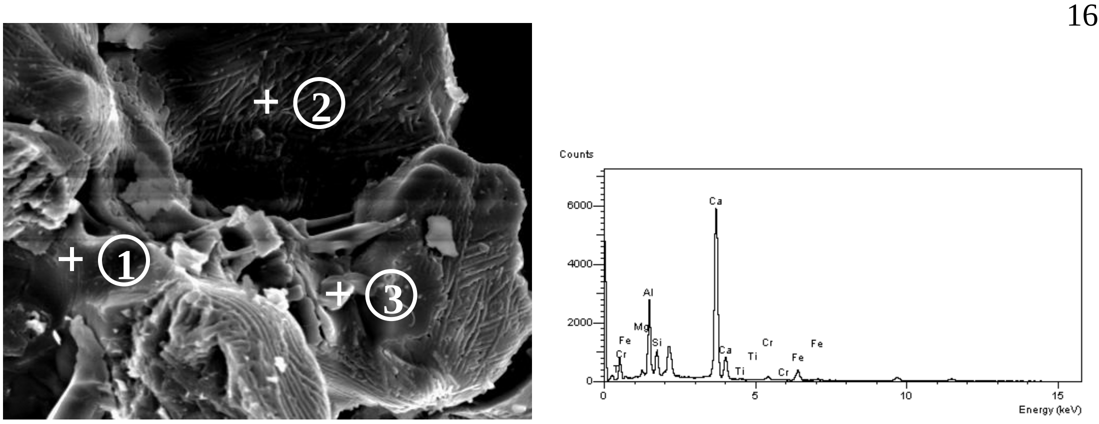


(e) The quantitative results of elements

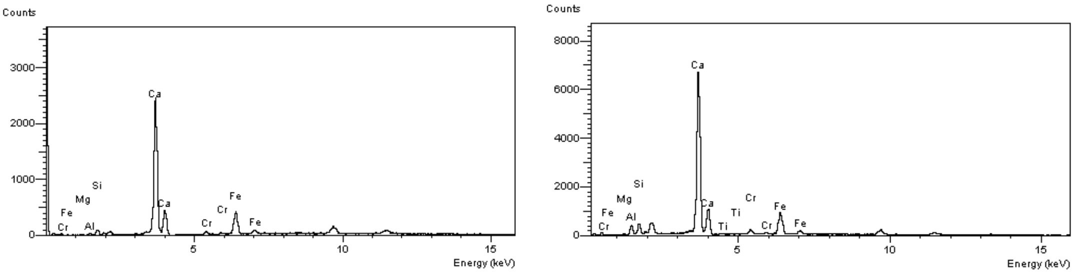
Figure E.4: Analysis of clinker phase with added Cr 5000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.12: The quantitative result of elements in the clinker phase with added Cr 5000 ppm.

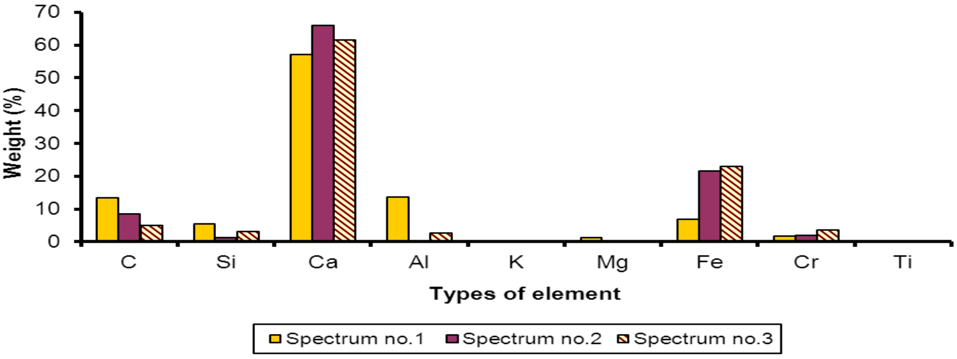
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.85	15.19	4.87
Si	12.86	3.91	7.87
Ca	73.09	77.13	78.53
Al	1.08	1.20	2.12
K	0.69	1.35	1.41
Fe	0	0	2.27
Cr	1.43	1.22	2.93
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

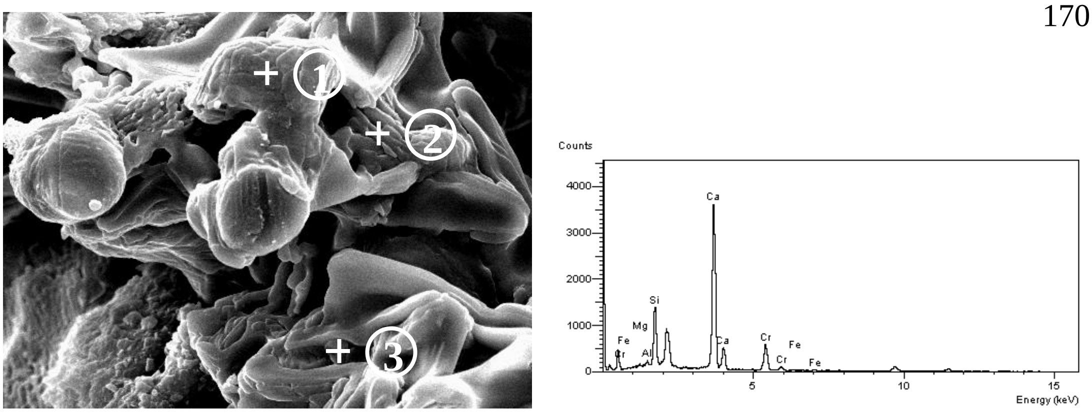


(e) The quantitative results of elements

Figure E.5: Analysis of clinker phase with added Cr 10000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

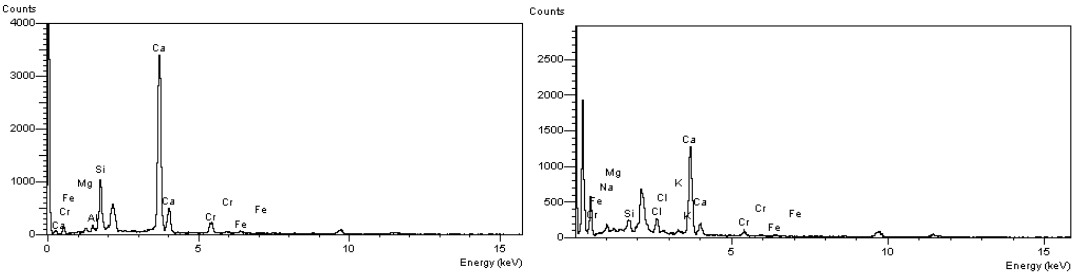
Table E.13: The quantitative result of elements in the clinker phase with added Cr 10000 ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	13.33	8.57	5.12
Si	5.55	1.25	3.15
Ca	57.01	66.05	61.61
Al	13.60	0.40	2.80
K	0.21	0	0
Mg	1.19	0.18	0.35
Fe	6.96	21.6	23.09
Cr	1.84	1.95	3.55
Ti	0.31	0	0.33
Total	100	100	100



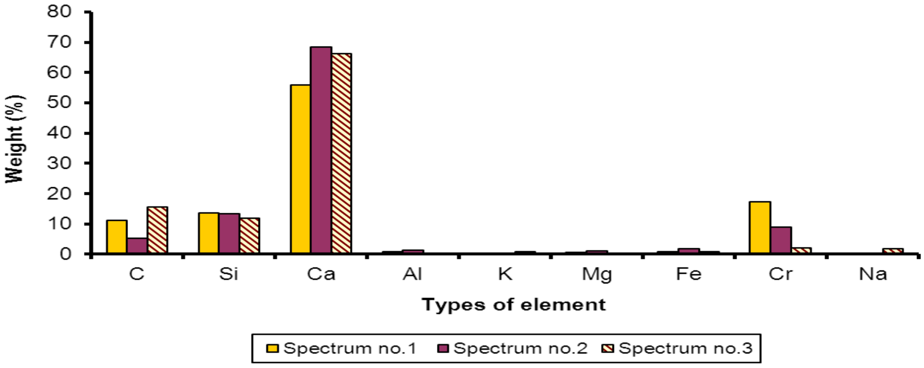
(a) Clinker phase 20kv x2000

(b) Spectrum no.1



(c) Spectrum no.2

(d) Spectrum no.3

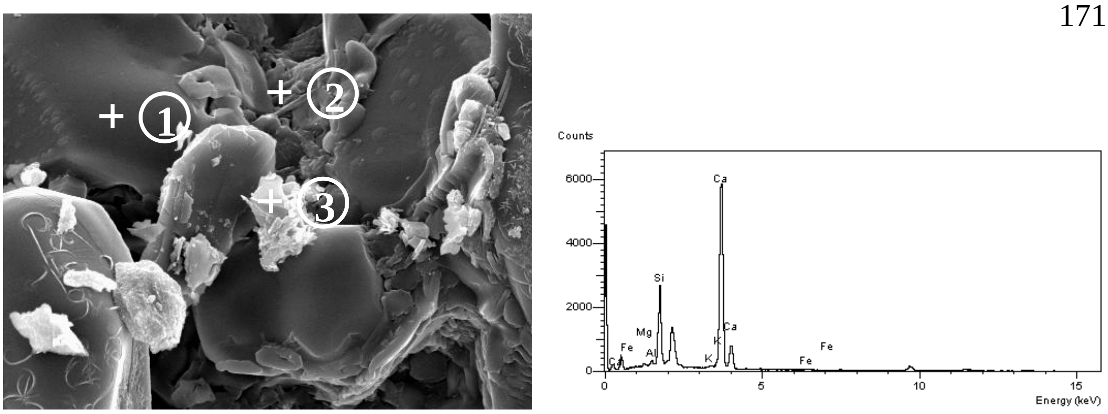


(e) The quantitative results of elements

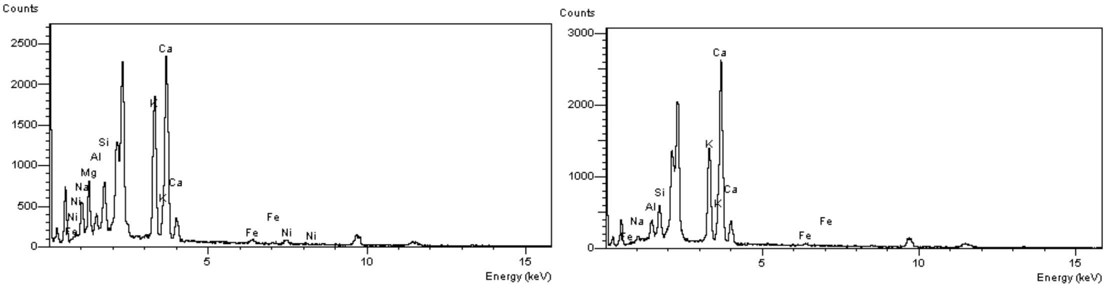
Figure E.6: Analysis of clinker phase with added Cr 20000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.14: The quantitative result of elements in the clinker phase with added Cr 20000 ppm.

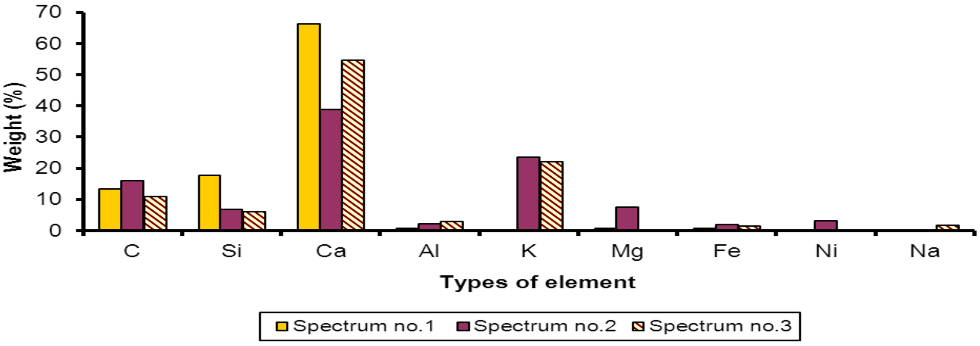
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	11.08	5.17	15.67
Si	13.54	13.36	11.98
Ca	55.9	68.45	66.19
Al	0.76	1.3	0
K	0	0	0.75
Mg	0.55	1.09	0.52
Fe	0.92	1.80	0.89
Cr	17.25	8.83	2.2
Na	0	0	1.80
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

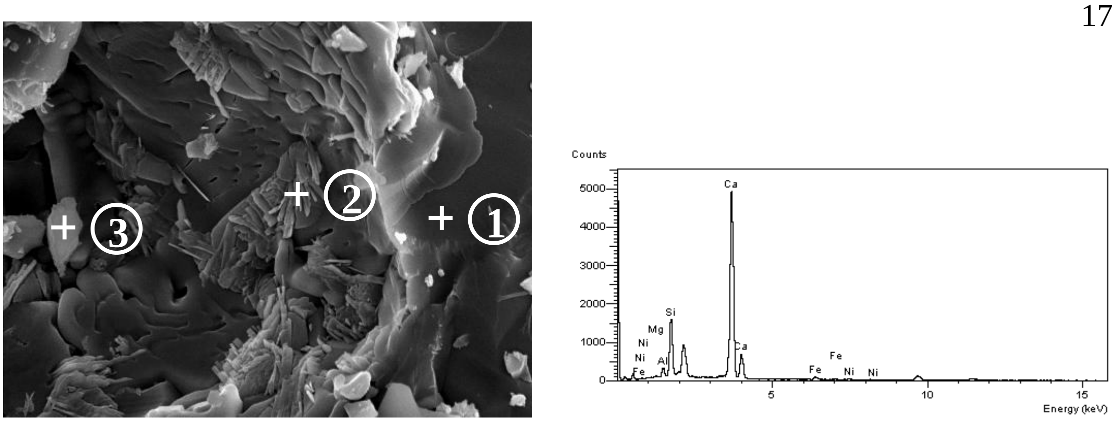


(e) The quantitative results of elements

Figure E.7: Analysis of clinker phase with added Ni 1000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

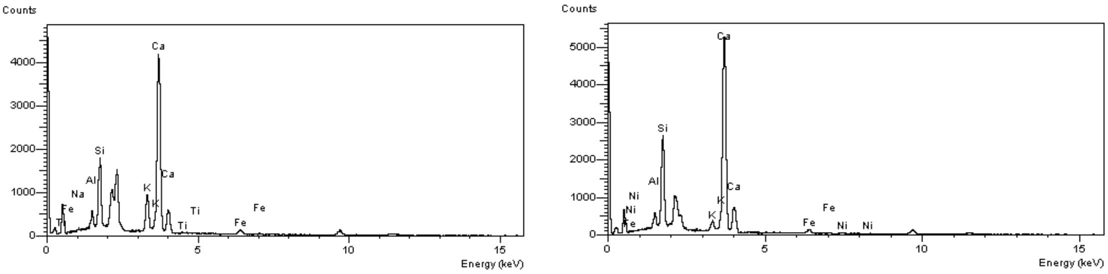
Table E.15: The quantitative result of elements in the clinker phase with added Ni 1000 ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	13.39	15.97	10.97
Si	17.65	6.84	6.08
Ca	66.44	38.8	54.73
Al	0.70	2.09	2.97
K	0.34	23.54	22.08
Mg	0.70	7.59	0
Fe	0.78	2.01	1.54
Ni	0	3.16	0
Na	0	0	1.63
Total	100	100	100



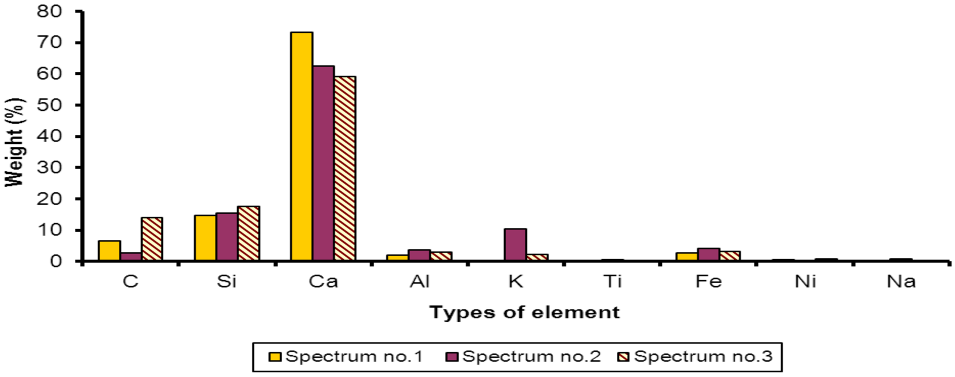
(a) Clinker phase 20kv x2000

(b) Spectrum no.1



(c) Spectrum no.2

(d) Spectrum no.3

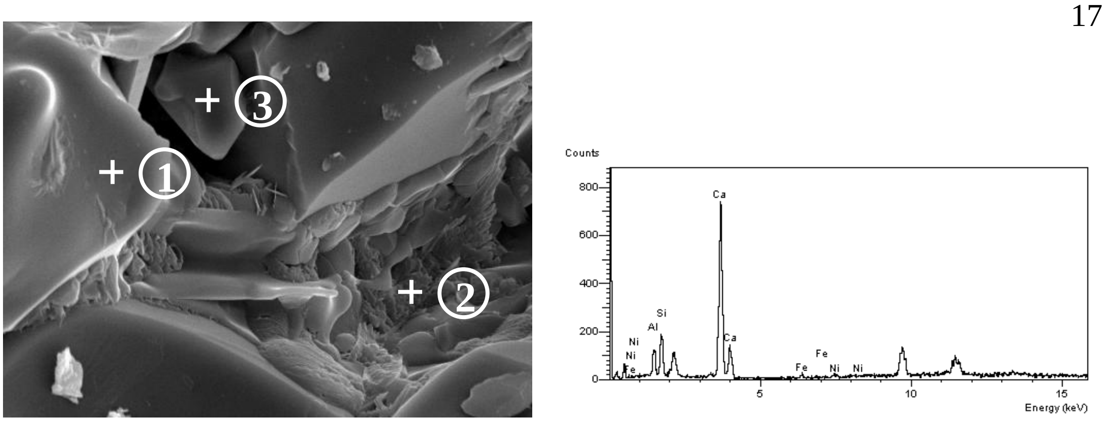


(e) The quantitative results of elements

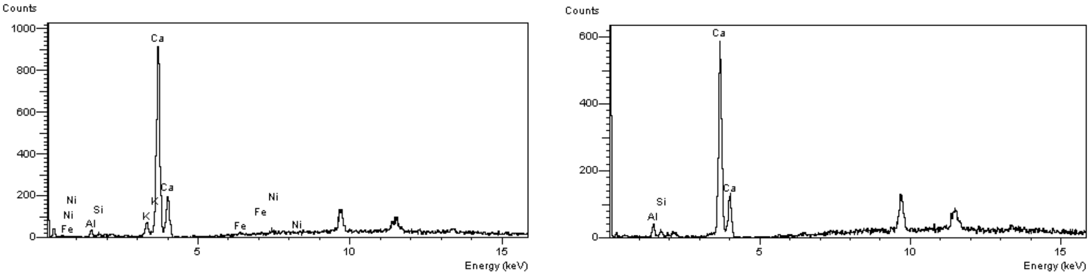
Figure E.8: Analysis of clinker phase with added Ni 5000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.16: The quantitative result of elements in the clinker phase with added Ni 5000 ppm.

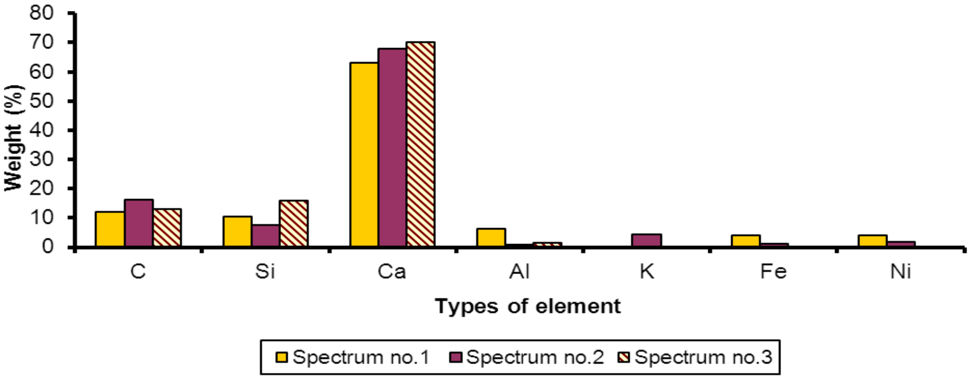
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	6.62	2.66	14.00
Si	14.71	15.55	17.68
Ca	73.34	62.50	59.04
Al	1.95	3.57	2.97
K	0	10.31	2.21
Ti	0	0.52	0
Fe	2.75	4.08	3.27
Ni	0.63	0	0.83
Na	0	0.81	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

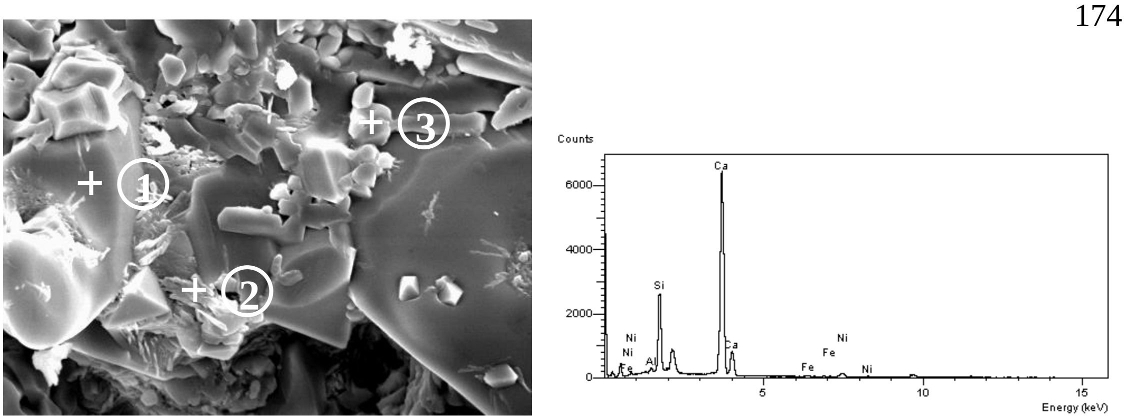


(e) The quantitative results of elements

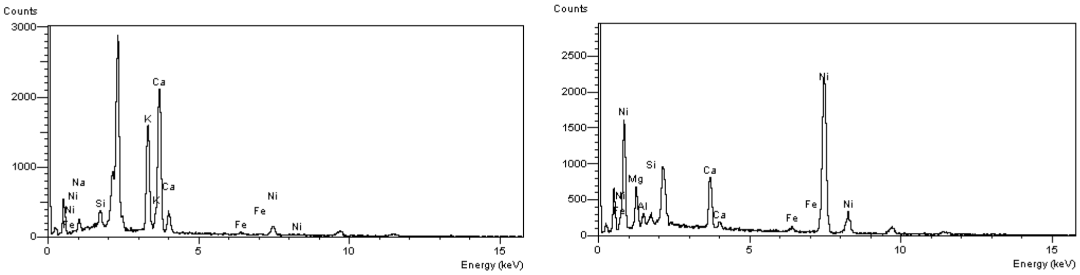
Figure E.9: Analysis of clinker phase with added Ni 10000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.17: The quantitative result of elements in the clinker phase with added Ni 10000 ppm.

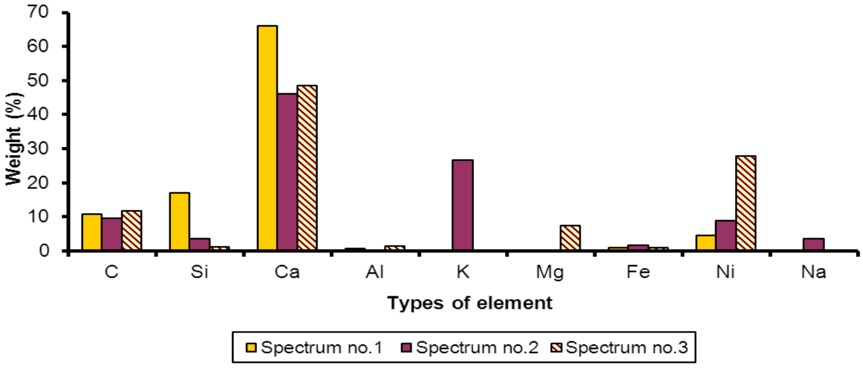
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	12.08	16.23	12.85
Si	10.46	7.50	15.77
Ca	63.11	68.04	69.92
Al	6.19	0.80	1.46
K	0	4.37	0
Fe	4.06	1.13	0
Ni	4.1	1.93	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

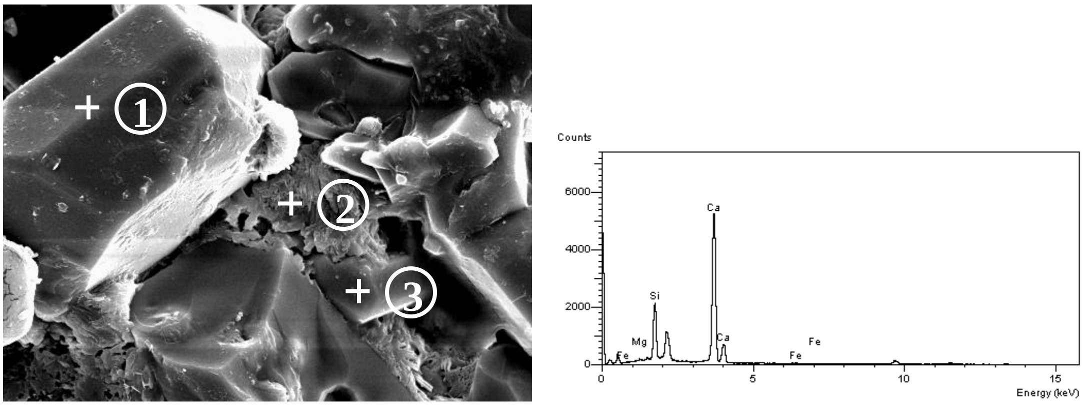


(e) The quantitative results of elements

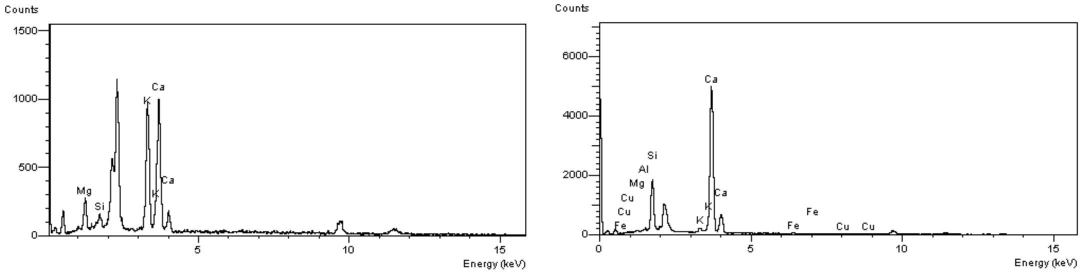
Figure E.10: Analysis of clinker phase with added Ni 20000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.18: The quantitative result of elements in the clinker phase with added Ni 20000 ppm.

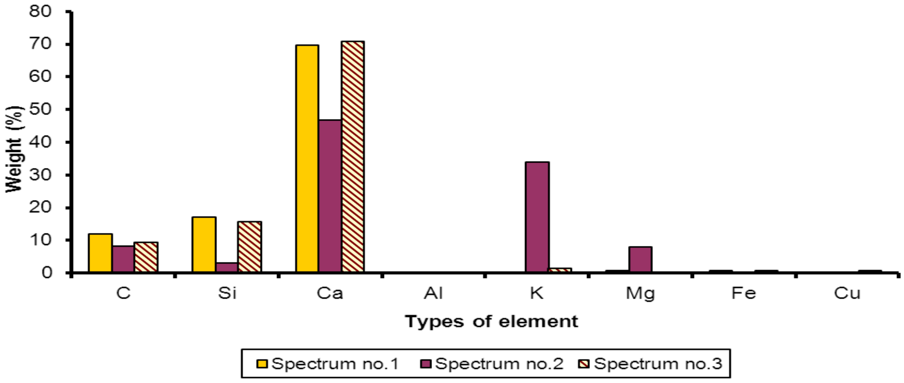
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.8	9.51	11.9
Si	16.99	3.63	1.39
Ca	66.15	46.04	48.63
Al	0.66	0	1.46
K	0	26.61	0
Mg	0	0	7.49
Fe	0.95	1.67	1.08
Ni	4.45	8.85	28.05
Na	0	3.69	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

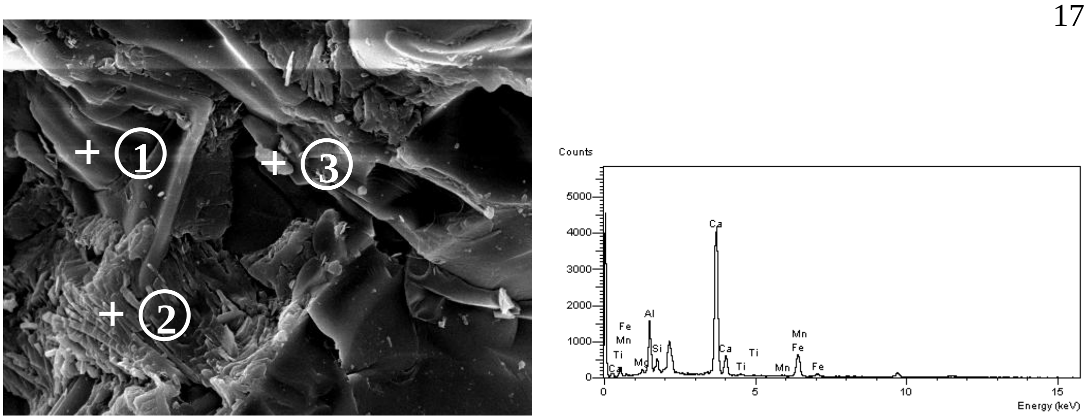


(e) The quantitative results of elements

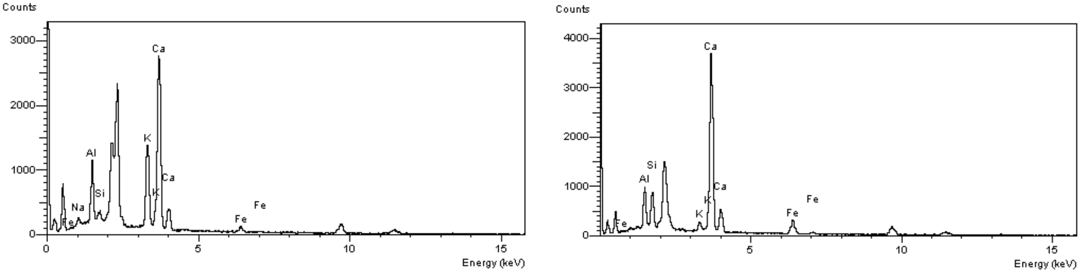
Figure E.11: Analysis of clinker phase with added Cu 1000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.19: The quantitative result of elements in the clinker phase with added Cu 1000 ppm.

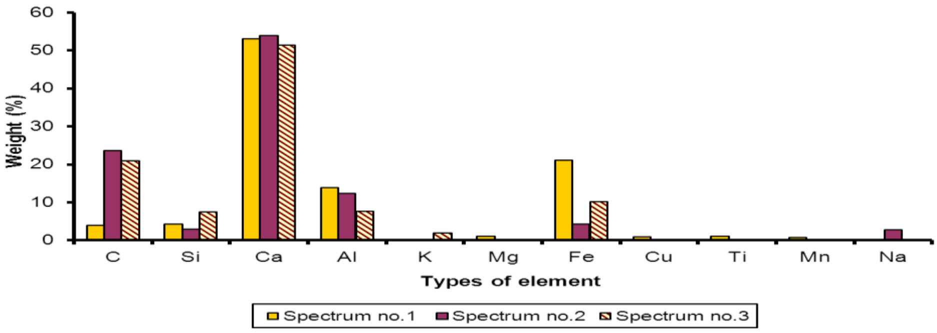
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	11.99	8.2	9.37
Si	16.98	3.09	15.73
Ca	69.63	46.75	70.85
Al	0	0	0.53
K	0	33.98	1.37
Mg	0.7	7.98	0.49
Fe	0.7	0	0.84
Cu	0	0	0.82
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

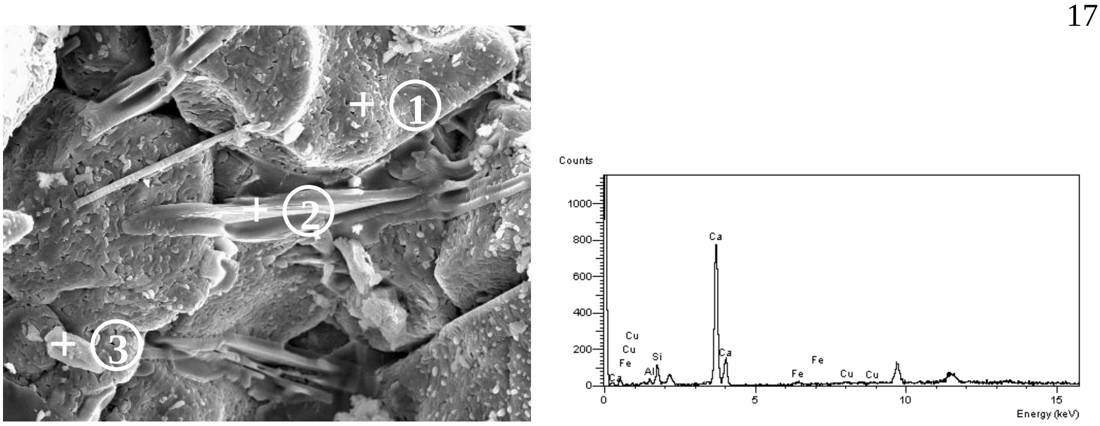


(e) The quantitative results of elements

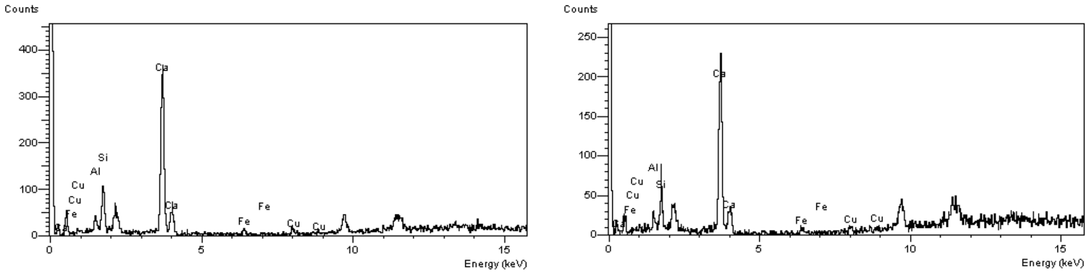
Figure E.12: Analysis of clinker phase with added Cu 5000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.20: The quantitative result of elements in the clinker phase with added Cu 5000 ppm.

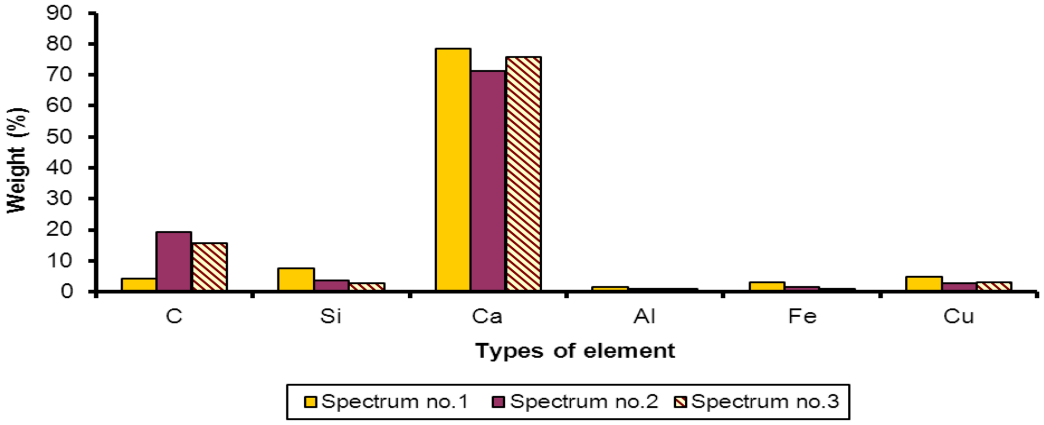
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	4.02	23.62	20.97
Si	4.34	3.01	7.58
Ca	53.05	53.92	51.5
Al	13.79	12.4	7.76
K	0	0	1.93
Mg	1.01	0	0
Fe	21.04	4.21	10.26
Cu	0.97	0	0
Ti	1.02	0	0
Mn	0.76	0	0
Na	0	2.84	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

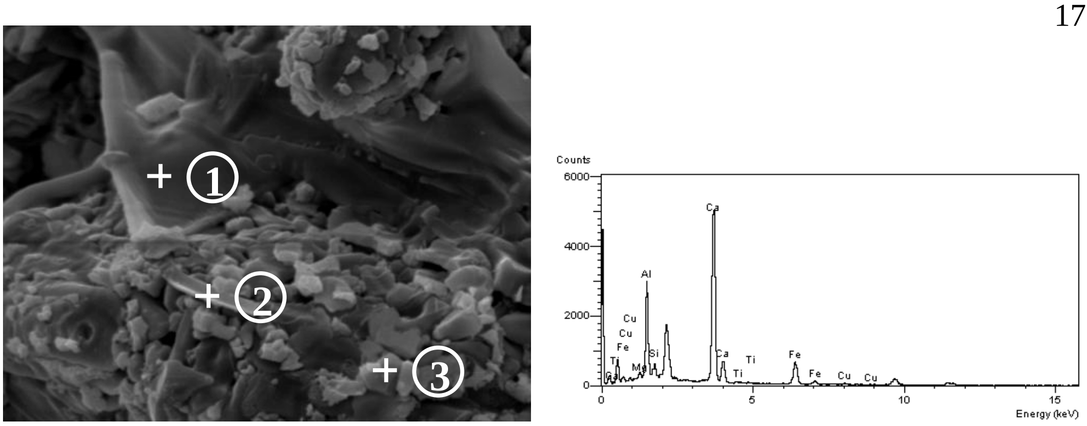


(e) The quantitative results of elements

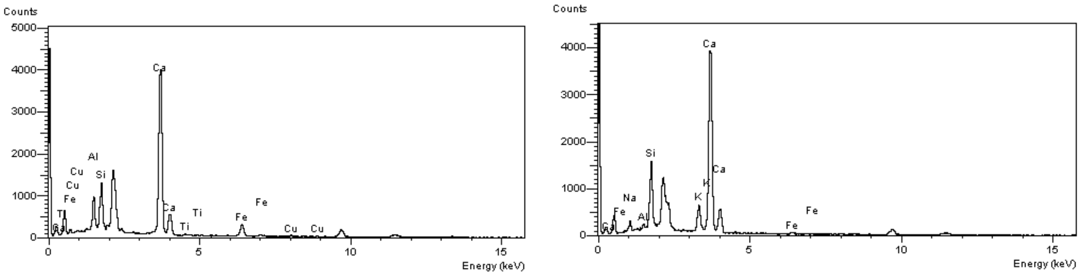
Figure E.13: Analysis of clinker phase with added Cu 10000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.21: The quantitative result of elements in the clinker phase with added Cu 10000 ppm.

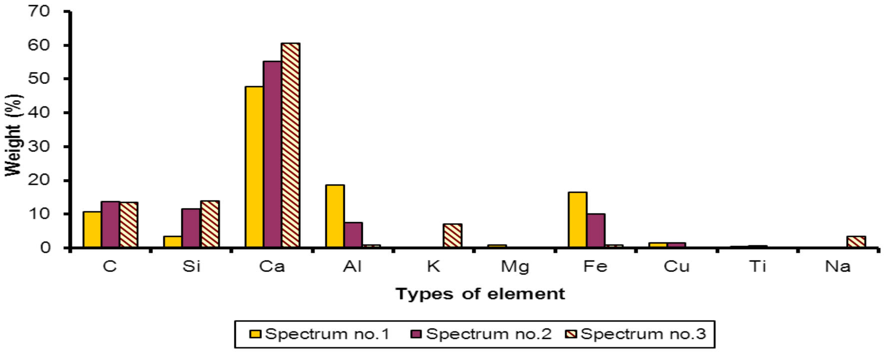
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	4.4	19.26	15.90
Si	7.65	3.68	2.74
Ca	78.57	71.37	76.02
Al	1.54	1.09	0.93
Fe	2.98	1.69	1.2
Cu	4.86	2.91	3.21
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

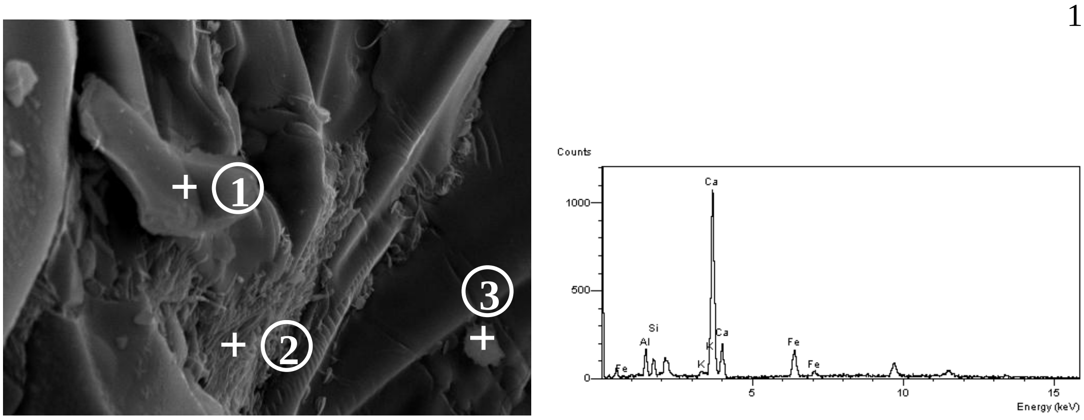


(e) The quantitative results of elements

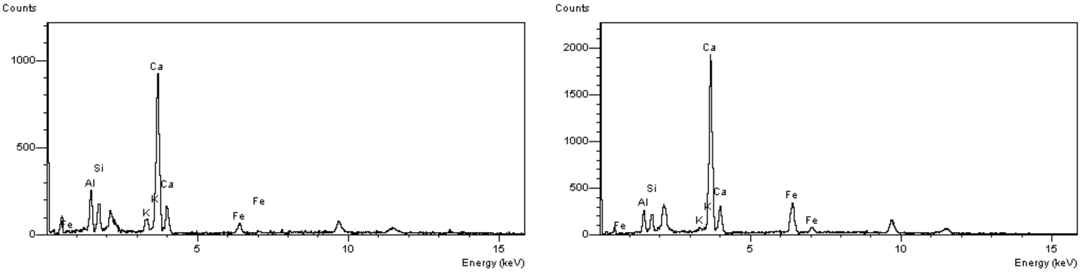
Figure E.14: Analysis of clinker phase with added Cu 20000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.22: The quantitative result of elements in the clinker phase with added Cu 20000 ppm.

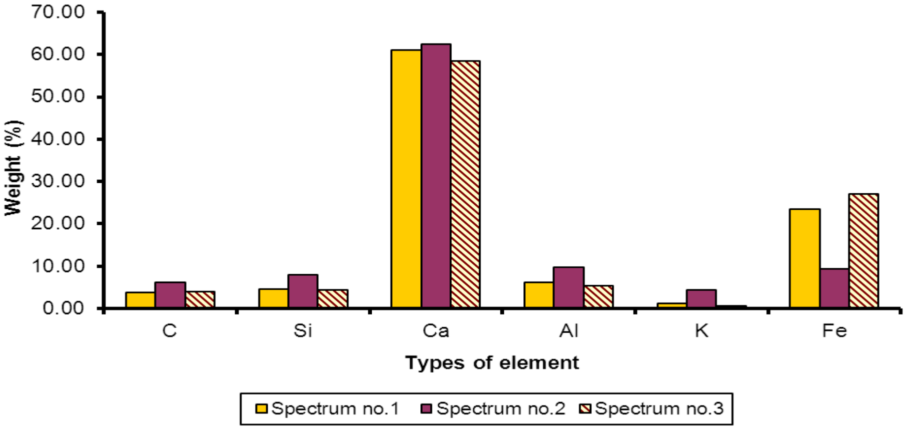
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.77	13.73	13.38
Si	3.51	11.57	13.96
Ca	47.78	55.16	60.56
Al	18.62	7.55	0.75
K	0	0	7.06
Mg	0.91	0	0
Fe	16.39	9.99	0.95
Cu	1.52	1.46	0
Ti	0.5	0.54	0
Na	0	0	3.34
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

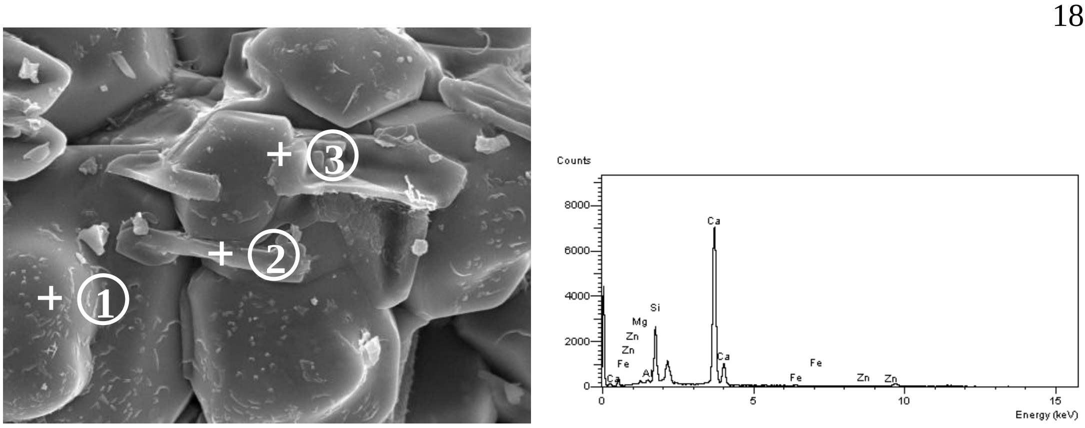


(e) The quantitative results of elements

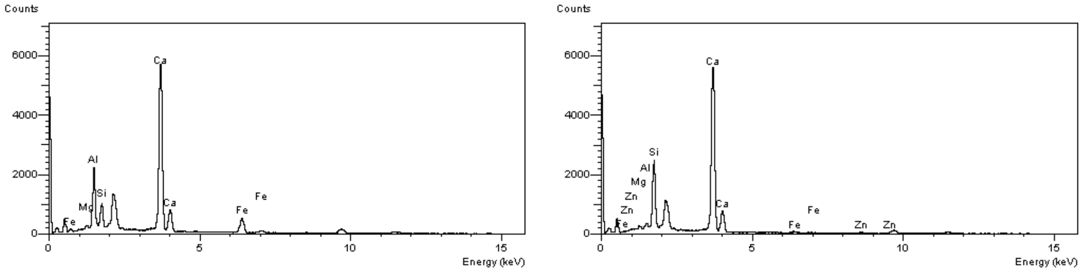
Figure E.15: Analysis of clinker phase with added Zn 1000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.23: The quantitative result of elements in the clinker phase with added Zn 1000 ppm.

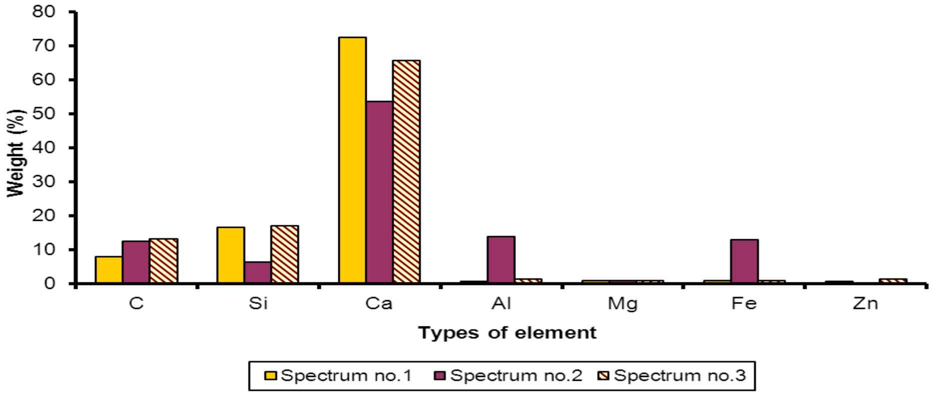
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	3.80	6.21	3.92
Si	4.56	7.91	4.48
Ca	60.97	62.49	58.51
Al	6.14	9.72	5.30
K	1.12	4.29	0.70
Fe	23.41	9.38	27.09
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

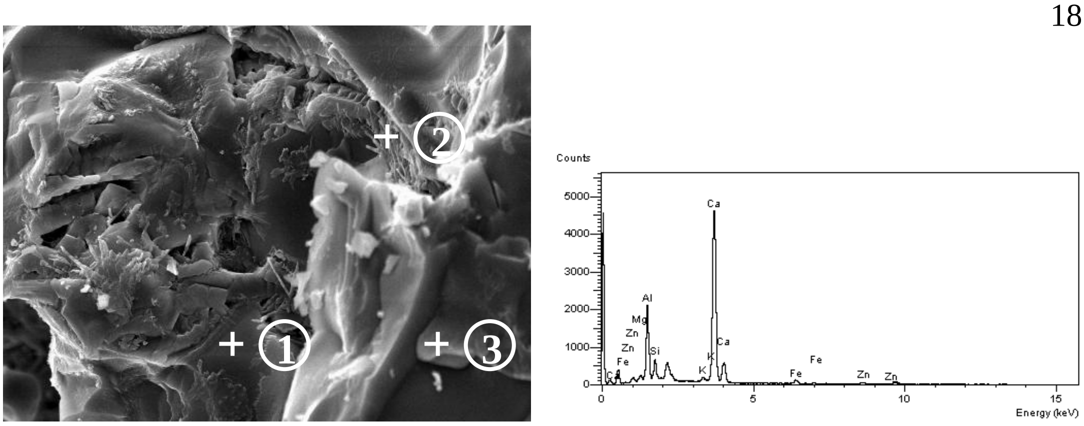


(e) The quantitative results of elements

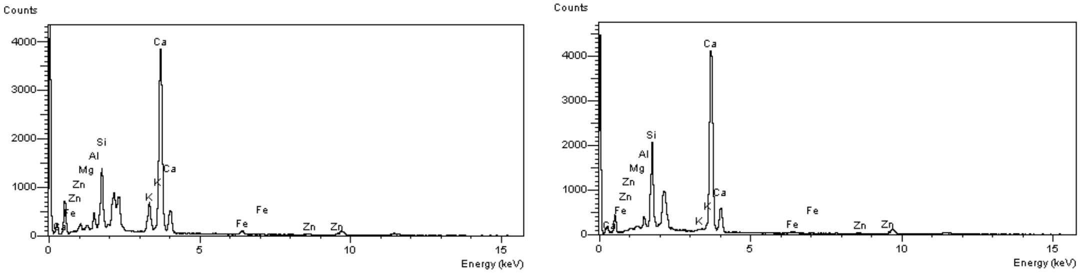
Figure E.16: Analysis of clinker phase with added Zn 5000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.24: The quantitative result of elements in the clinker phase with added Zn 5000 ppm.

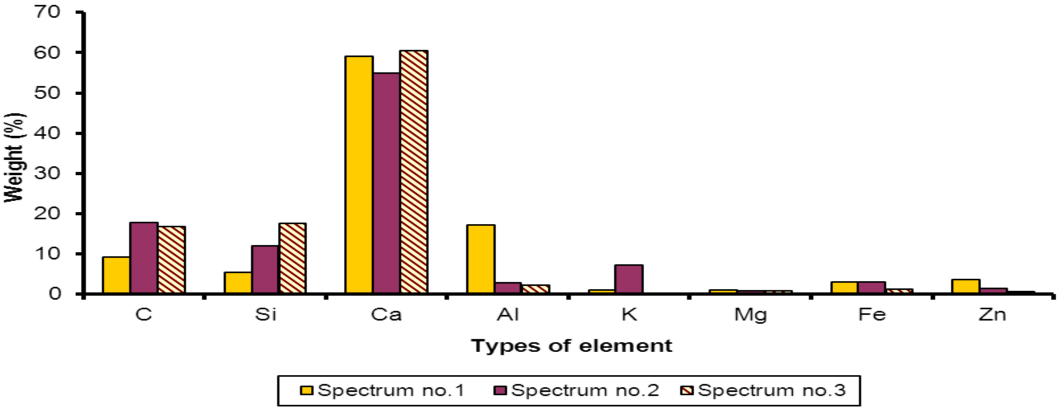
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	7.95	12.43	13.14
Si	16.54	6.31	16.91
Ca	72.52	53.72	65.56
Al	0.60	13.74	1.25
Mg	0.86	0.87	0.91
Fe	0.89	12.93	0.95
Zn	0.64	0	1.28
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

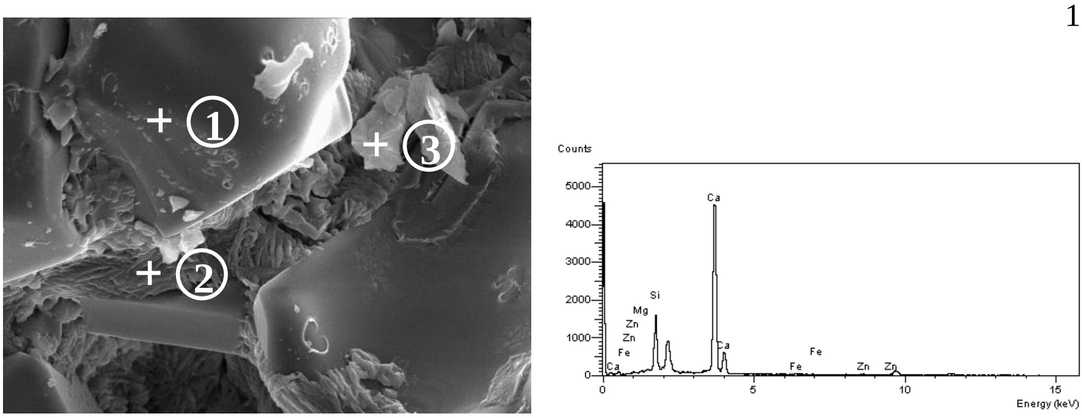


(e) The quantitative results of elements

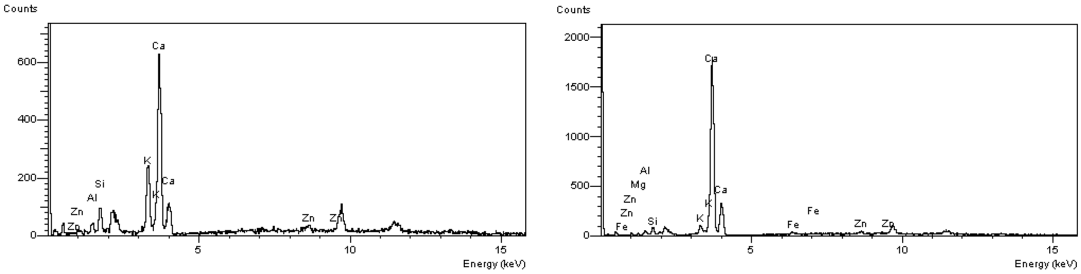
Figure E.17: Analysis of clinker phase with added Zn 10000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.25: The quantitative result of elements in the clinker phase with added Zn 10000 ppm.

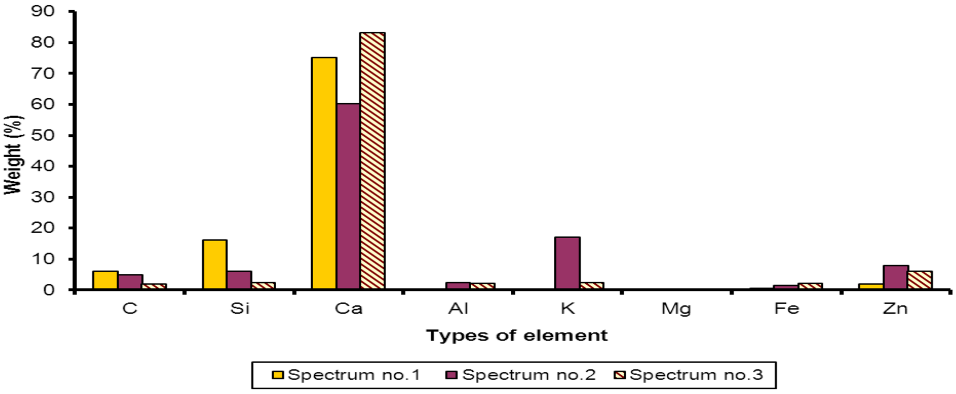
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	9.30	17.81	16.82
Si	5.51	11.95	17.57
Ca	59.10	54.91	60.52
Al	17.2	2.85	2.26
K	1.10	7.15	0.36
Mg	1.04	0.76	0.73
Fe	3.03	3.11	1.09
Zn	3.72	1.46	0.65
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

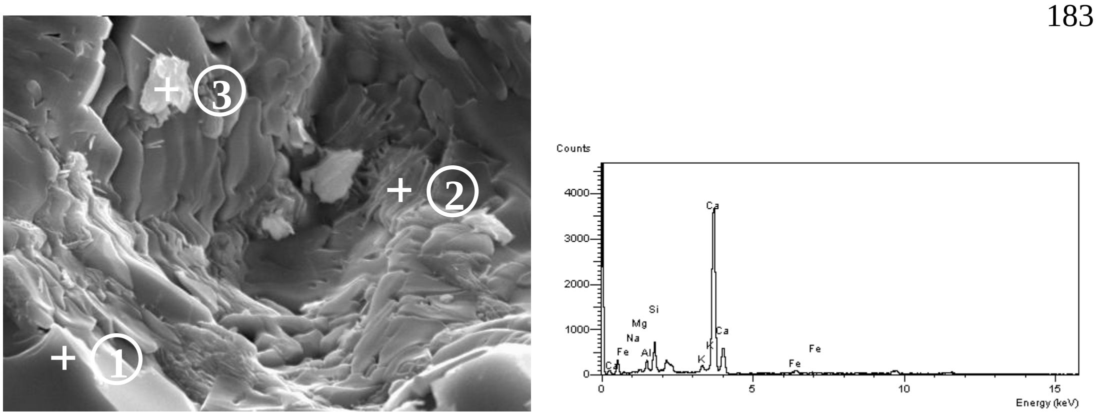


(e) The quantitative results of elements

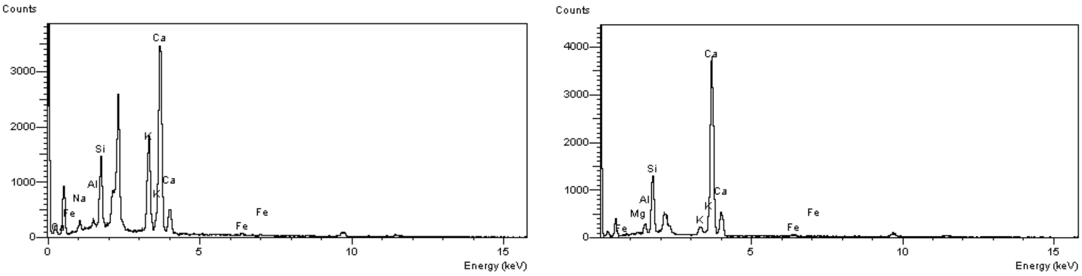
Figure E.18: Analysis of clinker phase with added Zn 20000 ppm: (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.26: The quantitative result of elements in the clinker phase with added Zn 20000 ppm.

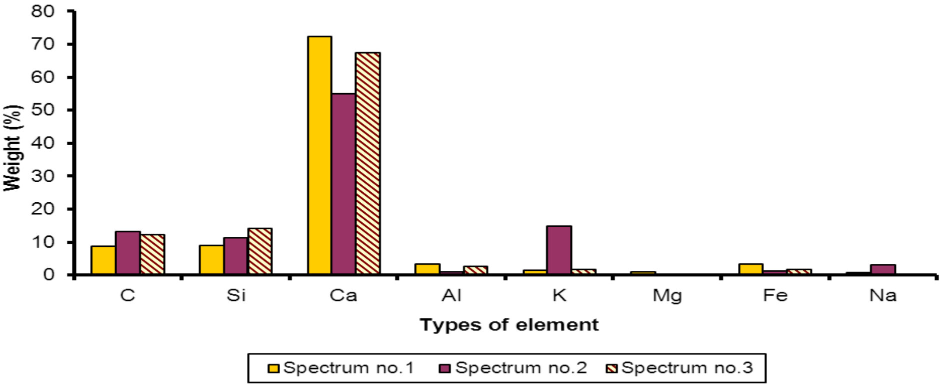
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	5.97	4.90	1.83
Si	16.08	6.06	2.32
Ca	75.06	60.33	83.02
Al	0	2.29	2.05
K	0	17.17	2.39
Mg	0.41	0	0.33
Fe	0.64	1.47	2.12
Zn	1.84	7.78	5.94
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

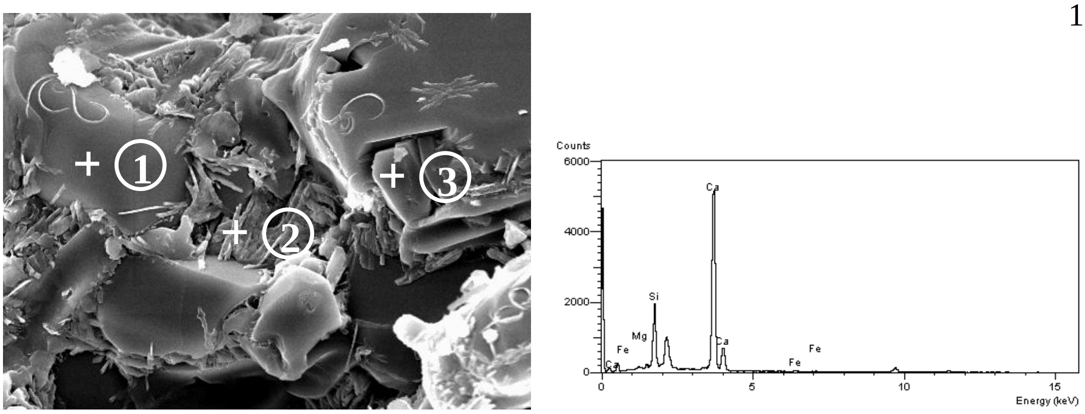


(e) The quantitative results of elements

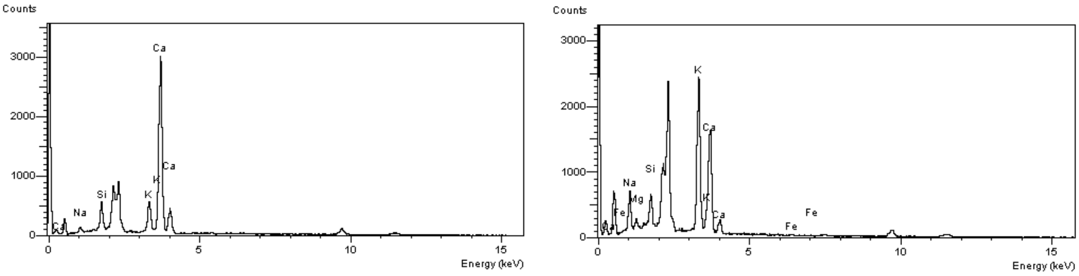
Figure E.19: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 500ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.27: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 500ppm.

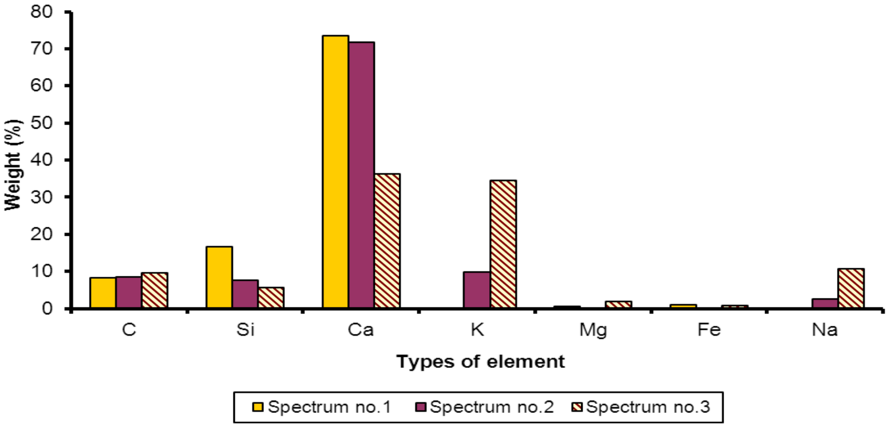
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	8.79	13.23	12.30
Si	8.90	11.31	14.00
Ca	72.36	54.99	67.43
Al	3.29	1.09	2.52
K	1.54	14.95	1.63
Mg	0.92	0	0.54
Fe	3.41	1.28	1.58
Na	0.79	3.15	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

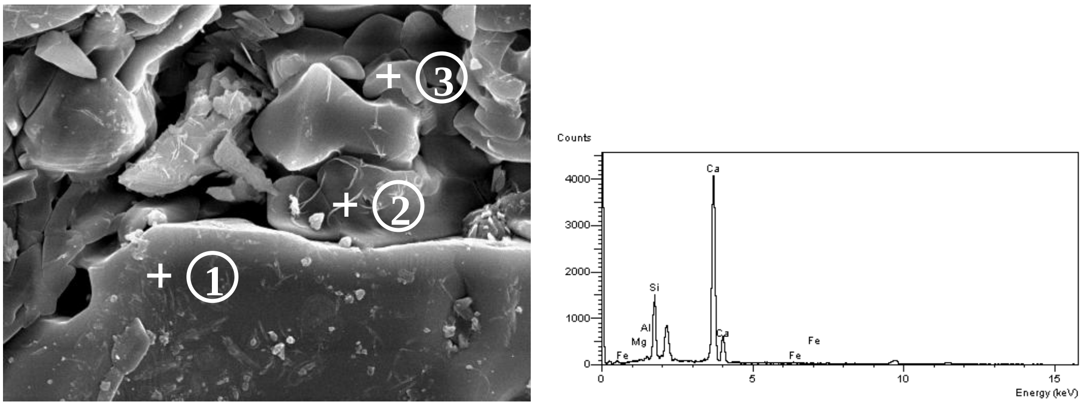


(e) The quantitative results of elements

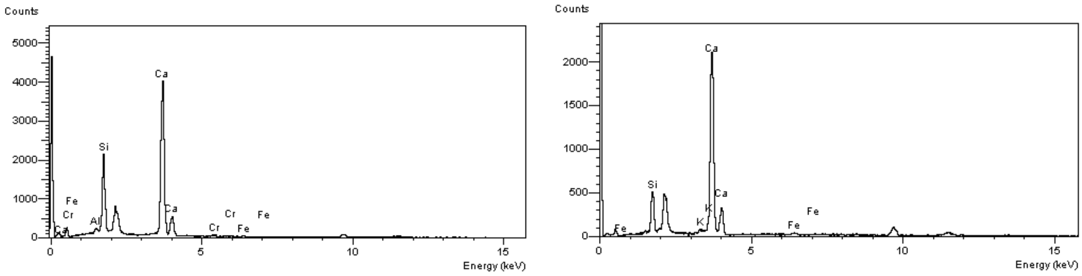
Figure E.20: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 3000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.28: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 3000ppm.

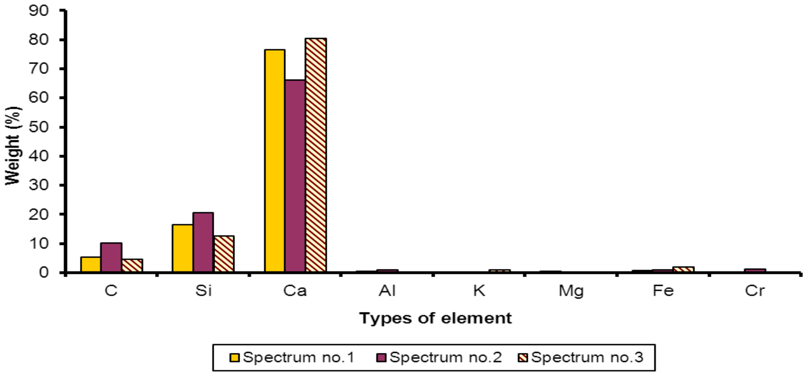
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	8.22	8.47	9.60
Si	16.58	7.65	5.81
Ca	73.5	71.65	36.32
K	0	9.79	34.7
Mg	0.66	0	2.02
Fe	1.04	0	0.82
Na	0	2.44	10.73
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

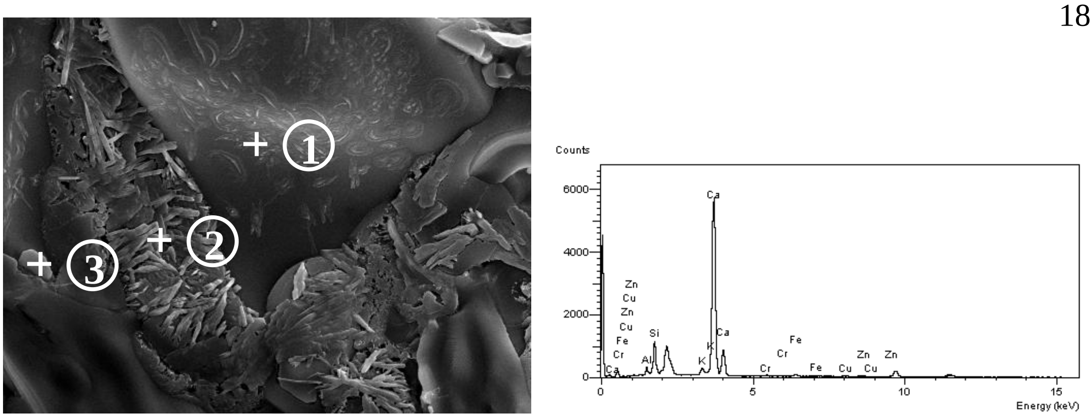


(e) The quantitative results of elements

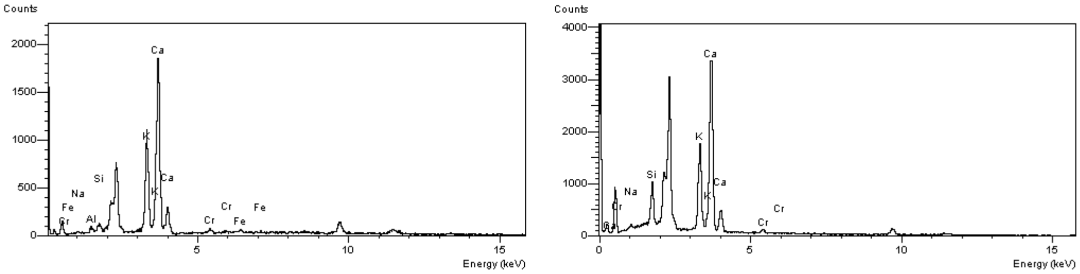
Figure E.21: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 5000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.29: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 5000ppm.

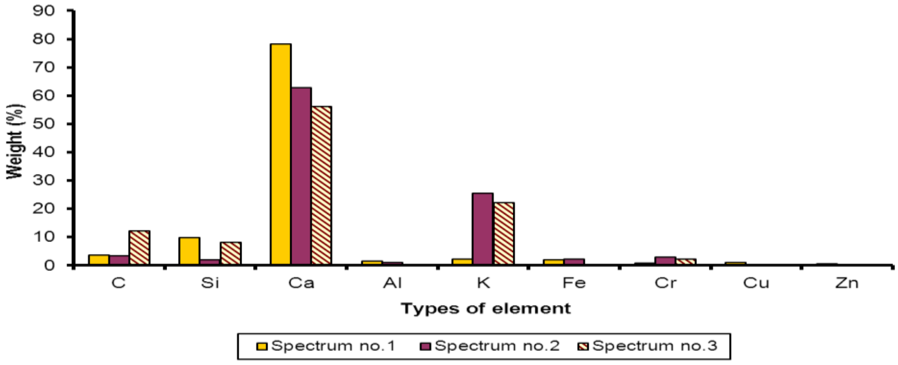
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	5.39	10.25	4.45
Si	16.46	20.63	12.38
Ca	76.46	66.19	80.38
Al	0.42	0.88	0
K	0	0	0.95
Mg	0.54	0	0
Fe	0.73	0.84	1.84
Cr	0	1.21	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

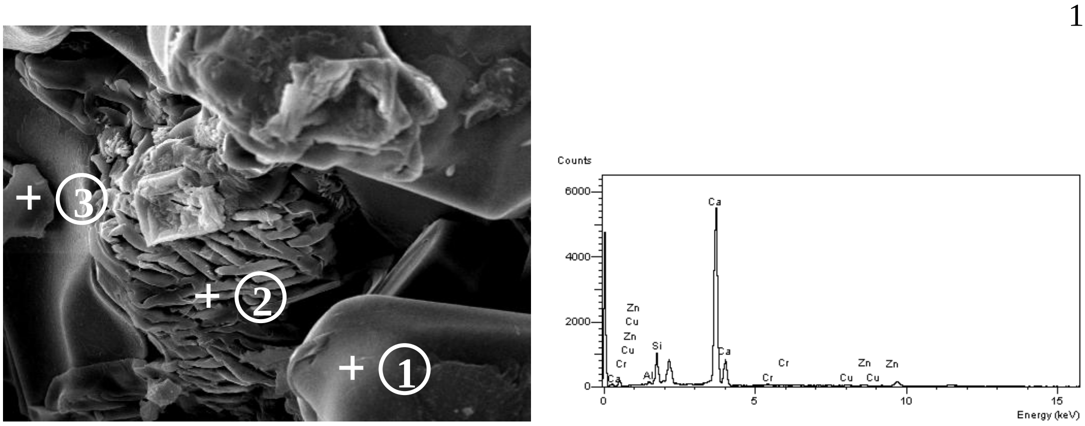


(e) The quantitative results of elements

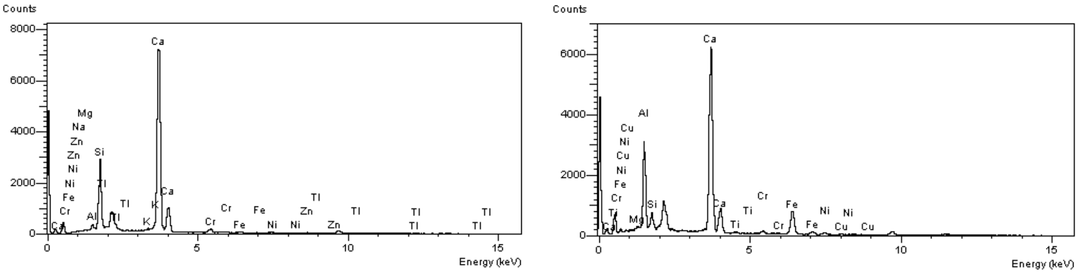
Figure E.22: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 10000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.30: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 10000ppm.

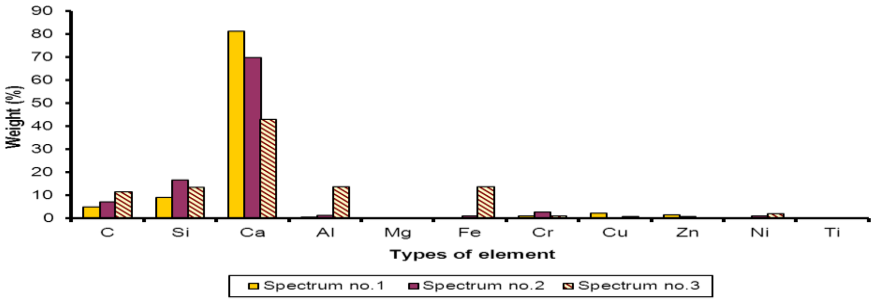
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	3.66	3.38	12.06
Si	9.88	1.98	7.97
Ca	78.21	62.77	55.94
Al	1.63	0.95	0
K	2.12	25.56	22.02
Fe	1.89	2.31	0
Cr	0.83	3.05	2.01
Cu	1.12	0	0
Zn	0.66	0	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

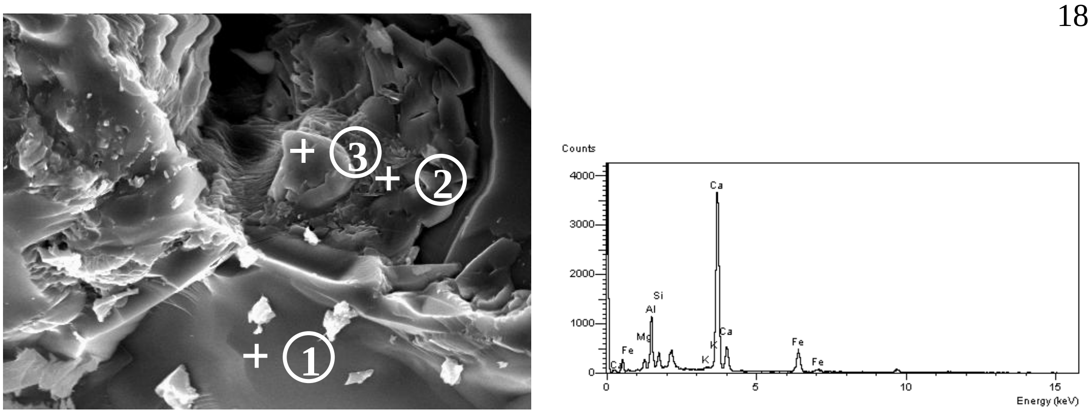


(e) The quantitative results of elements

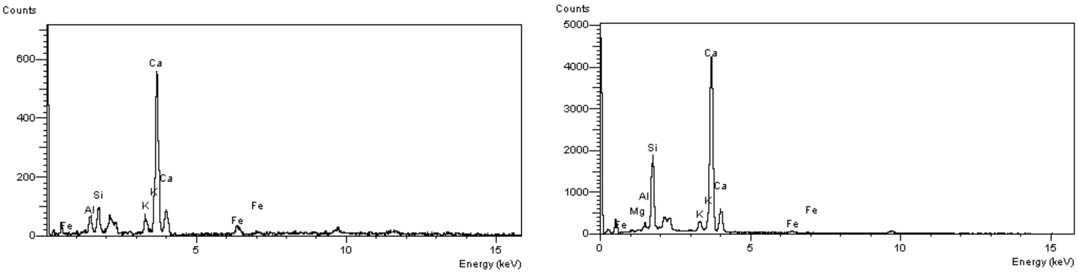
Figure E.23: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1 = 20000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.31: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:1:1:1= 20000ppm.

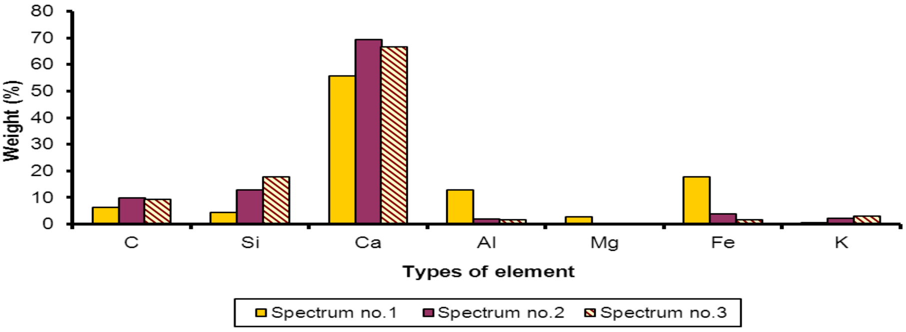
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	4.75	7.12	11.54
Si	9.08	16.55	13.39
Ca	81.12	69.68	42.86
Al	0.55	1.13	13.71
Mg	0	0.3	0.36
Fe	0	0.86	13.73
Cr	1.02	2.71	1.13
Cu	2.15	0	0.78
Zn	1.33	0.74	0
Ni	0	0.91	1.96
Ti	0	0	0.54
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

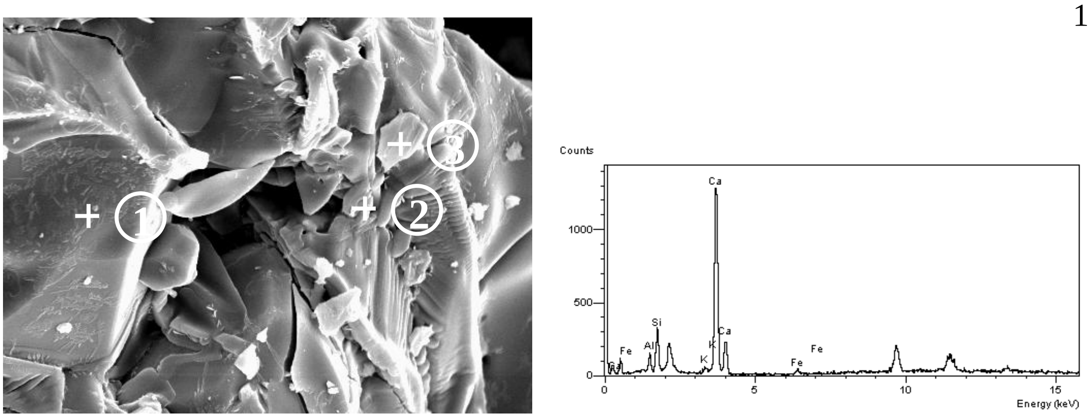


(e) The quantitative results of elements

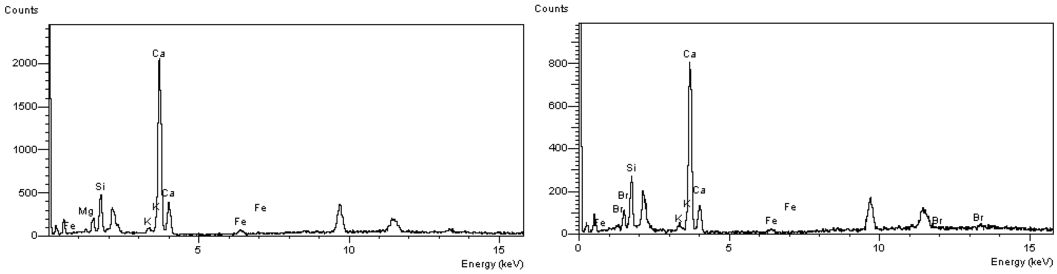
Figure E.24: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 500ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.32: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 500ppm.

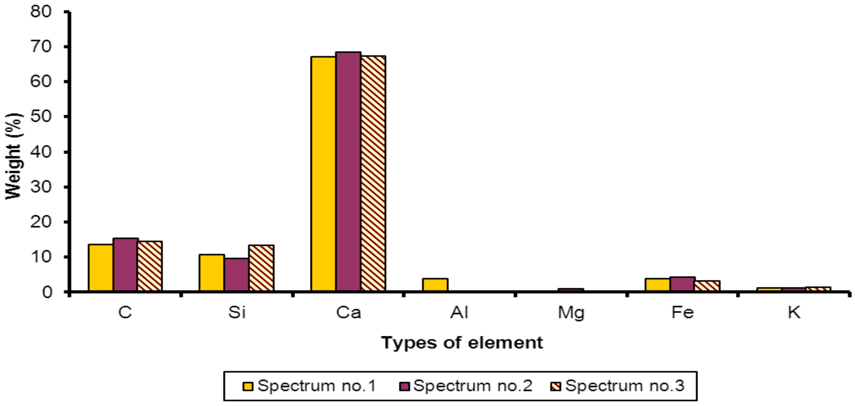
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	6.23	9.72	9.40
Si	4.43	12.93	17.63
Ca	55.61	69.36	66.54
Al	12.8	1.93	1.64
Mg	2.77	0	0.3
Fe	17.69	3.72	1.56
K	0.47	2.34	2.93
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

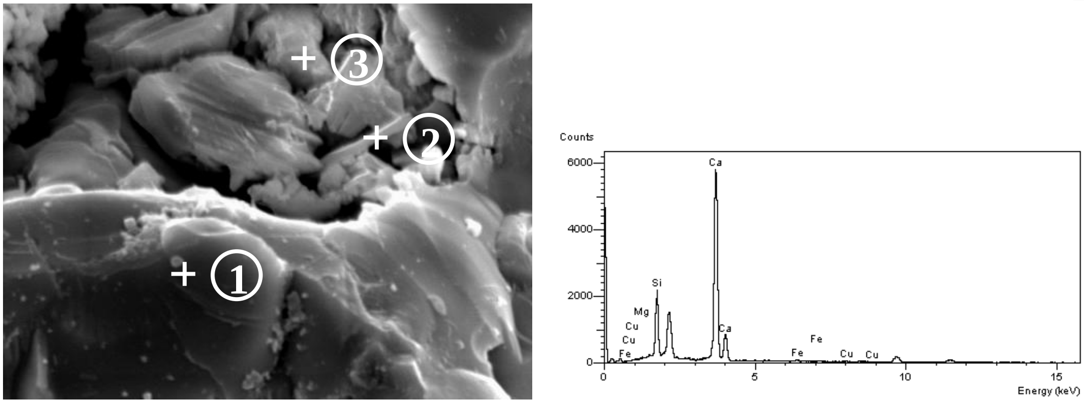


(e) The quantitative results of elements

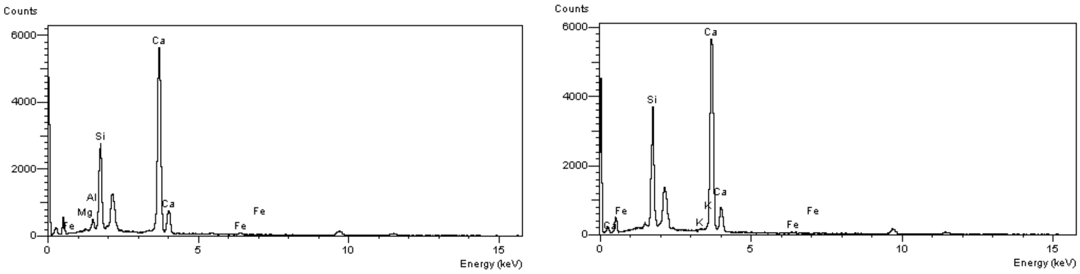
Figure E.25: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 3000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.33: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 3000ppm.

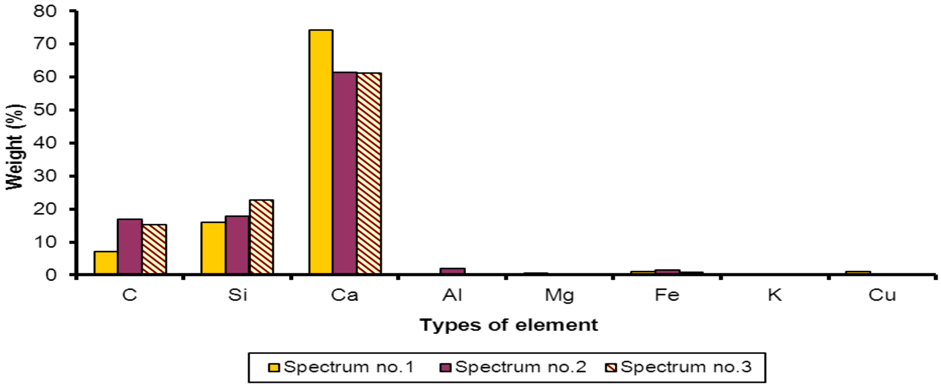
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	13.48	15.38	14.54
Si	10.72	9.58	13.41
Ca	67.06	68.48	67.3
Al	3.76	0	0
Mg	0	0.97	0
Fe	3.86	4.38	3.26
K	1.12	1.21	1.49
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

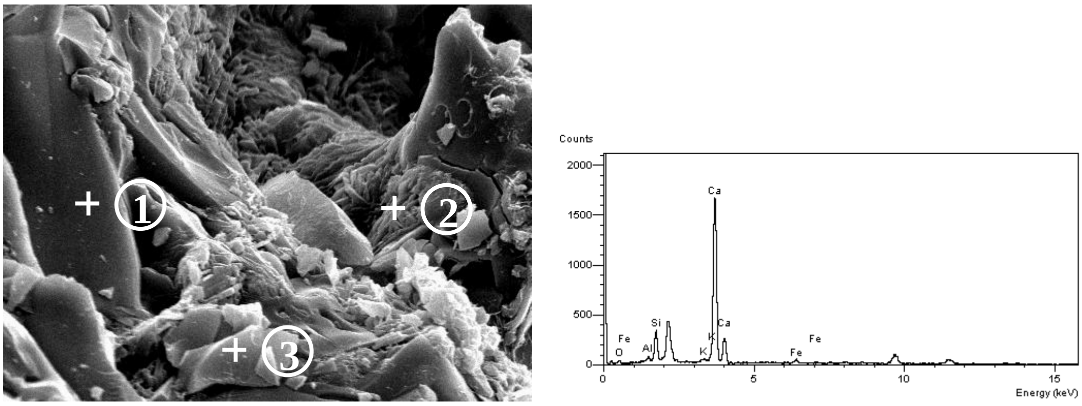


(e) The quantitative results of elements

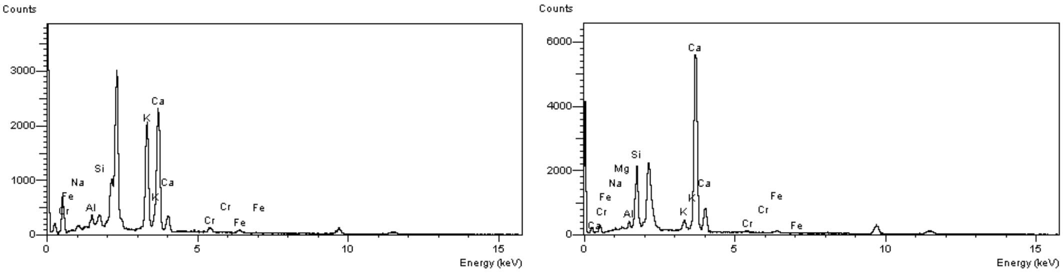
Figure E.26: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 5000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.34: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 5000ppm.

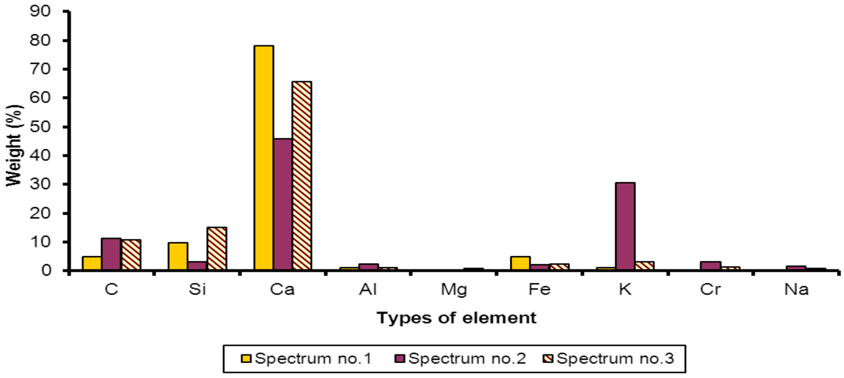
Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	7.21	16.88	15.27
Si	15.98	17.94	22.61
Ca	74.33	61.39	61.05
Al	0	1.88	0
Mg	0.47	0.45	0
Fe	0.99	1.46	0.69
K	0	0	0.38
Cu	1.02	0	0
Total	100	100	100



(a) Clinker phase 20kv x2000 (b) Spectrum no.1



(c) Spectrum no.2 (d) Spectrum no.3

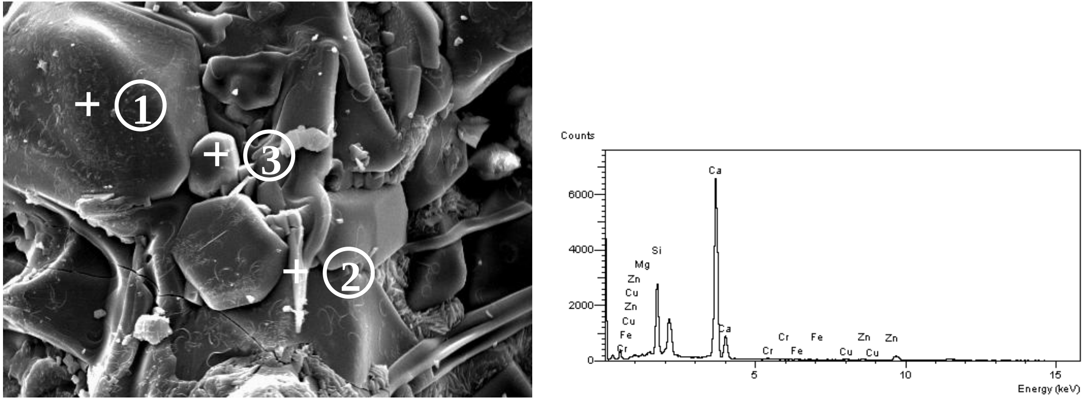


(e) The quantitative results of elements

Figure E.27: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 10000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

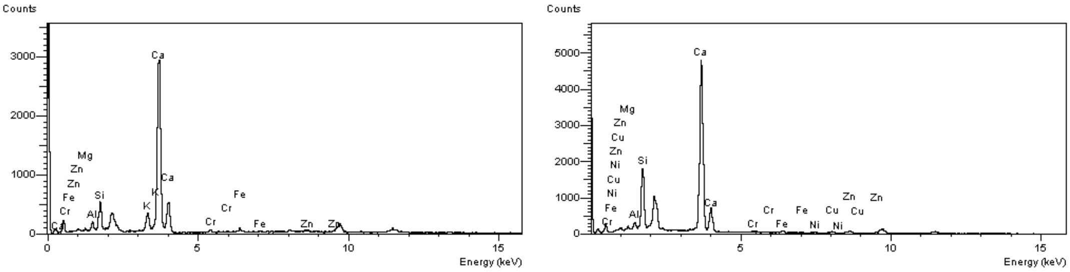
Table E.35: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 10000ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	4.93	11.28	10.58
Si	9.84	3.16	15.10
Ca	78.24	45.74	65.46
Al	1.17	2.32	0.96
Mg	0	0	0.62
Fe	4.77	2.11	2.32
K	1.05	30.56	3.1
Cr	0	3.23	1.19
Na	0	1.6	0.67
Total	100	100	100



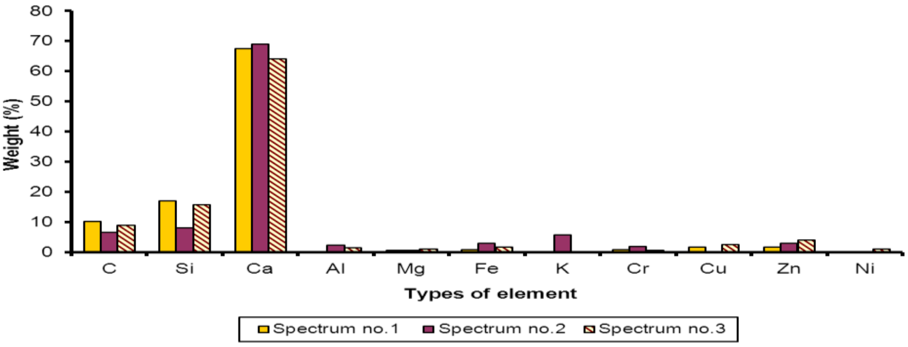
(a) Clinker phase 20kv x2000

(b) Spectrum no.1



(c) Spectrum no.2

(d) Spectrum no.3



(e) The quantitative results of elements

Figure E.28: Analysis of clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7 = 20000ppm (a) clinker phase, (b) spectrum no.1, (c) spectrum no.2, (d) spectrum no.3 (e) the quantitative results of elements

Table E.36: The quantitative result of elements in the clinker phase with added the combination of Ni:Cr:Cu:Zn =1:3:5:7= 20000ppm.

Element	Spectrum no.1 (weight, %)	Spectrum no.2 (weight, %)	Spectrum no.3 (weight, %)
C	10.17	6.48	8.73
Si	17.03	8.13	15.65
Ca	67.47	69.06	64.07
Al	0	2.23	1.29
Mg	0.49	0.62	0.99
Fe	0.77	2.89	1.49
K	0	5.76	0
Cr	0.78	1.96	0.53
Cu	1.62	0	2.46
Zn	1.67	2.87	3.83
Ni	0	0	0.96
Total	100	100	100

BIOGRAPHY

Name: Mr. Jenwit Krobthong

Date of Birth: September 22, 1975

Nationality / Race: Thai / Thai

Area of expertise: Environmental services, waste managements by cement kiln, recycle technology, sanitary and hazardous waste landfill technology, and environmental consultants.

Publication: DISTRIBUTIONS OF Cr, Ni, Cu and Zn IN HAZARDOUS WASTE CO-PROCESSING IN A PILOT-SCALE ROTARY CEMENT KILN, Journal of Applied Sciences, 2012, ISSN 1812-5654, DOI:10.3923/jas.2012

Education:

Degree	University / school	Year
M.ENG (Environmental Engineering)	Chiang Mai University	1998-2001
B.ENG (Environmental Engineering)	Chiang Mai University	1994-1998
Pre-University	Benjamamaharaj School Ubon	1991-1994
Secondary Education	Benjamamaharaj School Ubon	1988-1991

Work Experiences:

1/2009-9/2009: Executive Director
General Environmental Technology Co., Ltd.
10/2005-12/2008: Technical & Environmental Director
Teewasu Co., Ltd.
2/2001-9/2005: Environmental Health and Safety Manager (EHS Manager)
BYL Environmental Services Co., Ltd.
1/2000-1/2001: Project Superintendent
General Environmental Conservation Public Co., Ltd. (GENCO)