

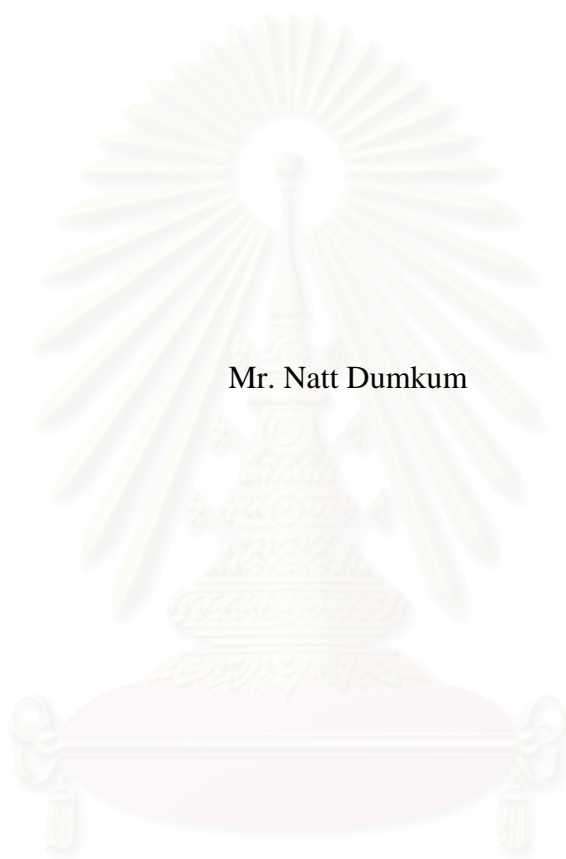
ผลกระทบทางกายภาพและเคมีของปูนซีเมนต์ที่ผสมกับอัตราส่วนที่แตกต่างกันของ
สังกะสี โครเมียมและนิกเกิลซึ่งผลิตโดยเตาเผาจำลองแบบหมุน



นาย ญัฐ คำจำ

สถาบันวิทยบริการ
วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PHYSICAL AND CHEMICAL CHARACTERISTICS OF CEMENT PRODUCED
WITH DIFFERENT RATIO OF Zn, Cr, AND Ni IN PILOT-SCALE ROTARY
CEMENT KILN



Mr. Natt Dumkum

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)

Graduate School

Chulalongkorn University

Academic Year 2008

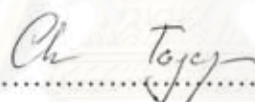
Copyright of Chulalongkorn University

Thesis Title	PHYSICAL AND CHEMICAL CHARACTERISTICS OF CEMENT PRODUCED WITH DIFFERENT RATIO OF Zn, Cr, AND Ni IN PILOT-SCALE ROTARY CEMENT KILN
By	Mr. Natt Dumkum
Field of study	Environmental Management
Thesis Advisor	Assistant Professor Manaskorn Rachakornkij, Ph.D.
Thesis Co-advisor	Viboon Sricharoenchaikul, Ph.D.


Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment
of the Requirements for the Master's Degree



..... Dean of the Graduate School
(Associate Professor Pornpote Piumsomboon, Ph.D.)

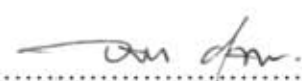
THESIS COMMITTEE


..... Chairperson
(Chantra Tongcumpou, Ph.D.)


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


..... Thesis Co-Advisor
(Viboon Sricharoenchaikul, Ph.D.)


..... Examiner
(Associate Professor Jin Anotai, Ph.D.)


..... External Examiner
(Mr. Thanit Pulivekin)

ฉันทู คำขำ : ผลกระทบทางกายภาพและเคมีของปูนซีเมนต์ที่ผสมกับอัตราส่วนที่แตกต่างกันของสังกะสี โครเมียม และนิกเกิลซึ่งผลิตโดยเตาเผาจำลองแบบหมุน. (PHYSICAL AND CHEMICAL CHARACTERISTICS OF CEMENT PRODUCED WITH DIFFERENT RATIO OF Zn, Cr, AND Ni IN PILOT-SCALE ROTARY CEMENT KILN) อ. ที่ปริกษาวิทยานิพนธ์หลัก: ผศ.ดร. มนัสกร ราชากรกิจ, อ.ที่ปริกษาวิทยานิพนธ์ร่วม: ดร.วิบูลย์ ศรีเจริญชัยกุล, 108 หน้า

การนำขยะจากโรงงานอุตสาหกรรมอื่น ๆ มาเผาพร้อมกับวัสดุคืบและเชื้อเพลิงในกระบวนการผลิตปูนซีเมนต์เป็นหนึ่งในวิธีการลดปริมาณการขยะในโรงงานอุตสาหกรรมรวมทั้งลดการใช้วัสดุคืบและเชื้อเพลิงรวมทั้ง แต่เนื่องจากในขยะที่นำมาใช้ในกระบวนการผลิตปูนซีเมนต์นั้นมีส่วนประกอบของโลหะหนักส่งผลกระทบต่อคุณสมบัติของปูนซีเมนต์ ในวิทยานิพนธ์วัสดุคืบที่ใช้ในการเผานั้นมีการผสมสารที่มีส่วนผสมระหว่างซิลิกากับดินเหนียวปริมาณ 2.5% เพื่อปรับค่าซิลิกา อะลูมินา และ การอ้อมตัวของหินปูนในวัสดุคืบให้เหมาะสมกับการเผาในเตาเผาจำลองแบบหมุนเนื่องจากเชื้อเพลิงที่ใช้เป็นแก๊ส LPG ซึ่งเวลาเผาไม่มีไถ่ลออกเพื่อไปลดปริมาณซิลิกา อะลูมินา และ การอ้อมตัวของหินปูนให้มีความเหมาะสมหลังการกระบวนการเผา จากผลการทดลอง ปริมาณที่เพิ่มขึ้นของโครเมียมในวัสดุคืบนั้นไม่มีผลกระทบต่อปริมาณน้ำหนักจากการตรวจสอบการเสียน้ำหนักจากความร้อนและกระบวนการเผาไหม้ที่ 800°C แต่ทว่าปริมาณที่เพิ่มขึ้นของโครเมียมหลังจากการเผาไหม้จนเป็นเม็ดปูนนั้นทำมีปริมาณของหินปูนอิสระเพิ่มขึ้น และยังไปลดปริมาณไครเคลเซียมซิลิเกต (C_3S) ในเม็ดปูนรวมทั้งลดกำลังรับแรงกดในก้อนซีเมนต์ ในเม็ดปูนนั้นพบว่าโครเมียมไปทำปฏิกิริยากับอะลูมิเนียมทำให้เกิดสารแคลเซียมอะลูมิเนียมโครเมียมออกไซด์ เช่นเดียวกับโครเมียมปริมาณที่เพิ่มขึ้นของนิกเกิลในวัสดุคืบ ไม่มีผลกระทบต่อการเสียน้ำหนักจากการตรวจสอบการเสียน้ำหนักจากความร้อนและกระบวนการเผาไหม้ที่ 800°C การเพิ่มปริมาณนิกเกิลนั้น ไปลดปริมาณหินปูนอิสระในเม็ดปูนและไปลดกำลังรับแรงอัดในก้อนซีเมนต์ นอกจากจากการตรวจสอบพบว่าในนิกเกิลได้ไปทำปฏิกิริยากับแมกนีเซียมจนเกิดสาร แมกนีเซียมนิกเกิลออกไซด์ ในเม็ดปูน จากการตรวจสอบการเสียน้ำหนักจากความร้อนและกระบวนการเผาไหม้ที่ 800°C พบว่าการเพิ่มสังกะสีในวัสดุคืบไม่มีผลกระทบในการเสียน้ำหนักจากการตรวจสอบความร้อนแต่ไปลดปริมาณน้ำหนักในกระบวนการเผาไหม้ที่ 800°C ปริมาณที่เพิ่มขึ้นของสังกะสีนั้น ไปลดปริมาณหินปูนอิสระแต่ไปเพิ่มปริมาณไครเคลเซียมซิลิเกตกับไครเคลเซียมซิลิเกตในเม็ดปูน ปริมาณสังกะสีที่เพิ่มขึ้นนั้น ไปเพิ่มกำลังรับแรงอัดของก้อนปูนซีเมนต์ในวันที่ 28 ของการทดลอง จากการตรวจสอบในเม็ดปูนพบว่าสังกะสีไปทำปฏิกิริยากับ เหล็ก แมงกานีส และ โครเมียม จนเกิดสาร ซิงค์ไอรอนแมงกานีสโครเมียมออกไซด์ นอกจากนี้ในการตรวจสอบการชะละลายของคลหะหนักพบว่าแม้จะเพิ่มปริมาณของโลหะหนักทั้งสามชนิดปริมาณที่ได้นั้นยังอยู่ในเกณฑ์มาตรฐานที่ทางกรมโรงงาน ได้ตั้งไว้

สาขาวิชา การจัดการสิ่งแวดล้อม
ปีการศึกษา 2551

ลายมือชื่อ นิสิต.....
ลายมือชื่อ อ.ที่ปริกษาวิทยานิพนธ์.....
ลายมือชื่อ อ.ที่ปริกษาวิทยานิพนธ์ร่วม.....

4989421220 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORDS: PILOT-SCALE ROTARY CEMENT KILN/CO-PROCESSING/
PHYSICAL AND CHEMICAL CHARACTERISTIC/AND MAXIMUM HEAVY
METAL CONCENTRATION

NATT DUMKUM: PHYSICAL AND CHEMICAL CHARACTERISTICS OF
CEMENT PRODUCED WITH DIFFERENT RATIO OF Zn, Cr, AND Ni IN
PILOT-SCALE ROTARY CEMENT KILN. ADVISOR: ASST. PROF.
MANASKORN RACHAKORNKIJ, Ph.D., CO-ADVISOR: VIBOON
SRICHAROENCHAikul, Ph.D., 108 pp.

Co-processing between waste and raw material in cement plant was the one method to reduced concentration of the waste and decreased consumption of raw material and fuel. However, the heavy metal in waste made the effect to cement properties. This study investigated the physical and chemical characteristics of various mixtures of cement clinker. The 2.5% of mixture between shale core and clay was added in the raw meal for made the samples suitable in burning process with one meter of the pilot-scale rotary cement kiln. From the study, different ratio of Cr in raw meal did not make the effect moisture content and loss on weight in ignition process. When compared with control, high concentration of Cr increased percent free lime but decreased percent C_3S and compressive strength in the clinker phase. Cr reacted with Al to get calcium aluminum chromium oxide. Likely to Cr, different ratio of Ni did not make in moisture content and loss on weight in ignition process of raw meal. In contrast, high concentration of Ni reduced percent free lime but increase compressive strength in clinker phase. Ni reacted with Mg to get Magnesium nickel oxide. High concentration of Zn in raw meal increased moisture content and loss on weight in ignition process of raw meal. High concentration of Zn reduced free lime in clinker phase. High concentration of Zn also increased concentration in both C_3S and C_2S . The Zn made the effect in setting time of cement mortar and created high compressive strength in 28 days. Zn reacted with other heavy metal included Fe, Mn, and Cr to get zinc iron manganese chromium oxide. From the leaching test, the all of different ratio of each three heavy metals still in the range when compared with Thai standard.

Field of Study: Environmental Management

Academic Year: ...2008.....

Student's Signature.....

Advisor's Signature.....

Co-Advisor's Signature.....

ACKNOWLEDGEMENTS

First of all, I would like to thank Assistant Professor Dr. Manaskorn Rachakornkij, my advisor and Dr. Viboon Sricharoenchaikul, my co-advisor for their valuable suggestions, guidance, and evaluation of this thesis. My gratitude is also owed to Dr. Chantra Tongcumpou and Associate Professor Dr. Jin Anotai, whom as defended committee member provided their advice on this thesis. The NCE-EHWM of Chulalongkorn University has provided me with a valuable education that I will take with me into the future

I am also grateful to Mr. Thanit Pulivekin, vice president of technical & engineering from the Siam City Cement Public Co., Ltd and the distinguish committee for favoring and approving this thesis study. I would like to thank Mr. Nattavude Kongmuang and the officers from Siam City Cement Public Co., Ltd for the value information they imparted to me about cement. They also permitted my use of their instrument to test the samples.

Next, I would like to thank Mr. Jenwit Krobthong, a Ph.D. student of the NCE-EHWM at Chulalongkorn University for teaching, helping, and encouraging me during my research. His guideline was insightful, as he was the on who designed the pilot-scale rotary cement kiln used in the study, which I must add was produced by Saraburi Machine Work Co., Ltd. I am grateful to them as well

Finally, I must express my deep gratitude to my family, close friends from the NCE-EHWM (Chulalongkorn University), SIIT (Thammasart University), and Bangkok Christian College; and special person for keeping up my morale though their care, and love for me while I studied; they especially help me through those challenging times.

CONTENTS

	Page
Abstract (in Thai).....	iv
Abstract (in English).....	v
Acknowledgements.....	vi
Table of contents.....	vii
List of Tables.....	x
List of Figures.....	xiv

CHAPTER

I	INTRODUCTION.....	1
	1.1 Objectives of the study.....	1
	1.2 Hypotheses.....	2
	1.3 Scope of the study.....	2
II	THEORETICAL BACKGROUND AND LITERATURE REVIEW.....	5
	2.1 Types of cement production processes.....	5
	2.2 Steps of cement production.....	5
	2.3 Chemical composition in Portland cement.....	8
	2.4 Simple elements and oxides in the cement phase.....	10
	2.5 Heavy metals in cement.....	11
	2.6 Basic instrument for analyzing cement.....	12
	2.7 Pilot- scale rotary kiln parts.....	16
	2.8 Physical and chemical properties of the heavy metals in the cement phase.....	17
III	METHODOLOGY.....	23
	3.1 Raw materials.....	23

CHAPTER	Page
3.2 Pilot-scale rotary cement kiln.....	23
3.3 Sample preparation.....	24
3.4 Clinker.....	25
3.5 Analyses of loss on ignition and moisture content.....	25
3.6 Analyses of the structure and chemical properties of samples by XRD, XRF, and SEM.....	26
3.7 Analysis of strength of the Portland cement by ASTM C109/C109M-05.....	26
3.8 Analysis Total Heavy Metals by Microwave Digestion Method 3050 B.....	27
3.9 Analysis leaching of heavy metal by Waste Extraction Test B.E. 2548 (WET).....	27
IV RESULT AND DISCUSSION.....	32
4.1 Sample preparation.....	32
4.2 Moisture content and LOI analyses.....	36
4.3 Burning in the pilot scale rotary cement kiln.....	38
4.4 The content of free lime.....	40
4.5 The content of chemical oxide and chemical mineral.....	42
4.6 Analysis of total heavy metal by EPA 3052B.....	46
4.7 The phase of heavy metal in the clinker that analyzed by XRD and SEM.....	47
4.8 Leaching test by WET B.E. 2548.....	56
4.9 Compressive strength.....	59

CHAPTER	Page
V CONCLUSION	63
5.1 Conclusions.....	63
5.2 Recommendation.....	64
REFERENCES.....	65
APPENDICES.....	69
APPENDIX A.....	70
APPENDIX B.....	76
APPENDIX C.....	79
BIOGRAPHY.....	108



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

Table		page
1.1	Concentration of heavy metal in the kiln feed	3
1.2	Concentrations of metal oxide input in kiln feed samples.....	3
1.3	Limit of heavy metal concentration from the Thai standards, 2005.....	4
1.4	Physical and chemical analysis.....	4
2.1	Chemical concentrations of minerals in clinker.....	6
2.2	Concentrations of chemical oxide in clinker.....	
2.3	The types of element can measure from line, and each wavelength as follow (Beckhoff, B.2006).....	13
2.4	Limit values set by authorities for cement plants individual permits.....	20
2.5	Maximum, minimum, and average concentration of heavy metals in raw meal, clinker, and Portland cement published by the VDZ in the year 2000.....	21
2.6	Concentration of heavy metals in clinker from the SCCC in May, 2007.....	21
2.7	Heavy metal in cement market in May 2007.....	22
2.8	Maximum concentration of heavy metal in waste was set by SCCC (Siam City Cement Co.).....	22
3.1	Properties of 6 g of cement for testing strength of cement sample....	26
3.2	Least compressive strength in specific times.....	27
4.1	Average percent of chemical composition of kiln feed from silo number 5 and 6, factory number 3.....	32
4.2	Average concentration of chemical composition in mixed kiln feed.....	33
4.3	The chemical composition of shale core, clay, and mixture of shale core and clay (25g:20g).....	34

Table	page
4.4	Concentration of chemical composition inside kiln feed after added 2.5% of mixture between shale core and clay.....34
4.5	Concentration of heavy metal in the raw meal control that analyzed by EPA 3052B and ICP..... 35
4.6	Analysis of concentration of Cr in the mixtures before burning in The- pilot scale rotary cement kiln by EPA 3052B and ICP.....35
4.7	Analysis of concentration of Ni in the mixtures before burning in the pilot scale rotary cement kiln by EPA 3052B and ICP.....35
4.8	Analysis of concentration of Zn in the mixtures before burning in the pilot scale rotary cement kiln by EPA 3052B and ICP.....35
4.9	Results of moisture content and loss on ignition percentages of kiln feed with different concentrations of Cr..... 36
4.10	Results of the moisture content and loss on ignition percentages of kiln feed at different concentrations of Zn.....37
4.11	Results of moisture content and loss on ignition percentages of kiln feed at different concentrations of Ni.....38
4.12	Analysis of chemical mineral in clinker that burning by static method..... 39
4.13	The result of clinker control from dynamic process.....39
4.14	Free lime in the clinker control and clinker samples.....41
4.15	Minerals composition in clinker samples by XRD.....43
4.16	Concentrations of chemical oxides, LSF, SM, and AM of the clinker samples at different concentrations of each heavy metals and control.....46
4.17	Analysis of concentration of heavy metal in the clinker control after burning in the pilot scale rotary cement kiln by EPA 3052B.....46
4.18	Analysis of concentration of Cr in the clinker after burning in the pilot scale rotary cement kiln by EPA 3052B.....46

Table	page
4.19	Analysis of concentration of Ni in the clinker after burning in the pilot scale rotary cement kiln by EPA 3052B.....47
4.20	Analysis of concentration of Cr in the clinker after burning in the pilot scale rotary cement kiln by EPA 3052B.....47
4.21	Concentrations of element in the clinker phase (Cr: 50,000 ppm), spectrum no.1..... 48
4.22	Concentrations of element in the clinker phase (Cr: 50,000 ppm), spectrum no.2.....49
4.23	Concentrations of element in the clinker phase (Cr: 50,000 ppm), spectrum no.3.....49
4.24	Concentrations of element in the clinker phase (Ni: 15,000 ppm), spectrum no.1.....51
4.25	Concentrations of element in the clinker phase (Ni: 15,000 ppm), spectrum no.2.....52
4.26	Concentrations of element in the clinker phase (Zn: 50,000 ppm), spectrum no.1.....54
4.27	Concentrations of element in the clinker phase (Zn: 50,000 ppm), spectrum no.2.....55
4.28	Concentrations of element in the clinker phase (Zn: 50,000 ppm), spectrum no.3.....55
4.29	Analysis of leaching behavior on the heavy metal in the clinker control after burning in the pilot- scale rotary cement kiln by WET.....57
4.30	Analysis of leaching behavior on the Cr in the clinker samples after burning in the pilot- scale rotary cement kiln by WET.....57
4.31	Analysis of leaching behavior on the Zn in the clinker samples after burning in the pilot- scale rotary cement kiln by WET.....58
4.32	Analysis of leaching behavior on the Ni in the clinker samples after burning in the pilot- scale rotary cement kiln by WET.....58

Table		page
4.33	Compressive strength of cement mortars with different concentrations of Cr.....	60
4.34	Compressive strength of cement mortars with different concentration of Ni.....	61
4.35	Compressive strength of cement mortars with different concentrations of Zn.....	62



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figure		page
2.1	Steps of the Portland cement production process.....	8
2.2	Structure of alite	9
2.3	Structure of belite.....	9
2.4	Structure of Tricalcium Aluminate.....	10
2.5	Photomicrograph of clinker (0.11mm.) that contain alite (blue), belite (orange), tricalcium aluminium (grey), and ferrit(white).....	10
2.6	Electronic transitions in a calcium atom.....	13
2.7	The example of heavy metal line that analyzed by XRF.....	14
2.8	XRD analysis of NAH +Al+ 4% mol of TiCl ₃ and NaAlH ₄ after milling 5h, 100 bar H ₂	15
3.1	Pilot- scale rotary cement kiln.....	23
3.2	Stainless capsule for adding kiln feed.....	24
3.3	The mixing machine.....	24
3.4	V-mix machine.....	25
3.5	The collected kiln feed.....	25
3.6	The new mixture between mixed kiln feed and 2.5% of mixed shale core and clay.....	25
3.7	Overall step of the EPA 3050 B method for analyzing total heavy metal.....	28
3.8	Overall of Waste Extraction Test B.E. 2548.....	29
3.9	Overall steps to produce the clinker control.....	30
3.10	Overall steps to produce the mixture samples.....	31
4.1	Moisture content and LOI of kiln feed with different concentration of Cr.....	37
4.2	Moisture content and LOI of kiln feed with different concentration of Zn.....	37
4.3	Moisture content and LOI of kiln feed with different concentration of Ni.....	38
4.4	The five position of crucible glasses for static burning process.....	39

Figure	page
4.5	Clinker inside the pilot-scale rotary cement kiln.....40
4.6	Thermocouple at the inlet part of the pilot-scale rotary cement kiln..... 40
4.7	Free lime content of the clinker samples with different concentrations of Zn.....42
4.8	Free lime content of the clinker samples with different concentrations of Cr.....42
4.9	Free lime content of the clinker samples with different concentrations of Ni.....42
4.10	Minerals in clinker samples with different concentrations of Cr..... 44
4.11	Minerals in clinker samples with different concentrations of Zn.....44
4.12	Minerals in clinker samples with different concentrations of Ni..... 45
4.13	Brown color of clinker that contain 5.0% wt of Zn..... 45
4.14	Analysis of Cr in the clinker phase by SEM-EDS..... 48
4.15	Percent weight of element in the clinker phase (Cr: 50,000 ppm), spectrum no.148
4.16	Percent weight of element in the clinker phase (Cr: 50,000 ppm), spectrum no.2..... 49
4.17	Percent weight of element in the clinker phase (Cr: 50,000 ppm), spectrum no.3..... 50
4.18	Analysis of Cr in clinker phase by XRD.....50
4.19	Analysis of Ni in the clinker phase by SEM-EDS.....51
4.20	Percent weight of element in the clinker phase (Ni: 15,000 ppm), spectrum no.1 51
4.21	Percent weight of element in the clinker phase (Ni: 15,000 ppm), spectrum no.2..... 52

Figure	page
4.22	Analysis of Ni in clinker phase by XRD..... 53
4.23	Analysis of Zn in the clinker phase by SEM-EDS..... 54
4.24	Percent weight of element in the clinker phase (Zn: 50,000 ppm), spectrum no.1.....54
4.25	Percent weight of element in the clinker phase (Zn: 50,000 ppm), spectrum no.2.....55
4.26	Percent weight of element in the clinker phase (Zn: 50,000 ppm), spectrum no.3.....56
4.27	Analysis of Zn in clinker phase by XRD..... 56
4.28	The leaching behavior of Cr in samples.....57
4.29	The leaching behavior of Zn in samples.....58
4.30	The leaching behavior of Ni in samples.....59
4.31	Compressive strength of cement mortars with different Cr concentrations.....60
4.32	Compressive strength of cement mortars with different Ni concentration61
4.33	Compressive strength of cement mortars with different Zn concentrations.....62

Chapter I

INTRODUCTION

At present, reduction of industrial wastes is necessary to decrease the demand for raw production materials and protect the environment. The cement industry collects waste from other types of factories to produce cement clinker (Taweekitwanit, 2004). Wastes that contain hydrocarbon structures or organic structures, and untreatable wastewater are among the types of wastes that are reused as raw material. Along with reducing the needs for capital and fuel, reutilization of wastes, decreases landfill waste concentrations, and increase energy conservation are the reasons to bring wastes from other types of industry for cement production process.

The sources of heavy metals in cement are raw materials and alternative fuels that come from industrial wastes (Taweekitwanit, 2004). Heavy metal contaminated wastes include galvanic sludge from the electroplating industry, sludge from the metal plating industry, and ash from used oil. Heavy metals can change the characteristics of cement; for example, they can change the color of the cement, and decrease or increase the strength of the cement (Sprung, 1985). It depends on quantity of heavy metals in the cement.

The major purpose of this study will be to investigate the effects of heavy metal in the physical and chemical characteristics of cement produced by a pilot-scale rotary cement kiln. Nickel, chromium, and zinc in the oxide form will be added into the kiln feed to produce clinker. The concentrations of metal oxide to be added into the kiln feed to get the concentration of metal ion similar to the input value will come from calculation. The input value of each of the three heavy metals will come from standards and literature. After that, the structures and characteristic of the clinker will be analyzed by XRD, XRF, ICP, and SEM. The strength of the cement product will be tested by ASTM C109/C109M-05. Total Digestion Method 3052 will be used for leaching tests and the result will be compared with the Notification of the Ministry of Industry BE 2548

This study will try to determine the maximum concentrations of heavy metals that can be contained within raw materials that do not impact the physical and chemical compositions of the cement and environment. At most, the results from this thesis can establish a minimum initial concentration of heavy metals in cement that would classify it as hazardous waste. Moreover, the initial concentration value from this thesis could be adapted and applied to waste from industries that contribute their raw materials for cement production process.

Objective

1. To examined physical and chemical characteristics of the selected heavy metal in the raw material and clinker.
2. To analyze physical and chemical properties of cement produced in a pilot-scale rotary kiln.

Hypothesis

Increase in concentration of zinc ions in cement can improve strength of cement but little effect to free lime. Increase in concentration of chromium ions would reduce strength of cement but raise concentration of free lime. Concentrations of nickel are little influence both in strength and free lime.

Scope of work

1. Ni, Cr, and Zn were the three types of heavy metal that were mixed with the raw material for producing clinker. All of the heavy metals were in the metal oxide form.
2. A pilot- scale rotary kiln is the instrument that was used to produce the cement clinker using dry process.
3. Before burning the mixture samples, the samples were evaporated in an oven at 100°C to remove the moisture.
4. The sample mixture for each sample was 10 kg. There were an approximate 40% loss from the burning process.
5. The mix ratio of each heavy metal is shown in the table 1. These ratios came from the Siam City Cement Public Co and the literature review.
6. Because of the prices of this three types of heavy metals are high, approximations of the concentrations of each of three types of metal oxide will be added into the kiln feed to make the concentrations of metals ions similar to values in Table 1.1 using the following formula:

$$\text{Concentration of metal oxide} = \frac{(\text{concentration of metal ion} \times \text{molecular weight})}{\text{Atomic weight}}$$

The results from the calculation for each of three types of heavy metals are according with the value in Table 1.2.

7. ICP, SEM, XRF, XRD, and microwave digestion were the instruments that were used for analyzing the characteristics of the heavy metal in the raw material and clinker.
8. Total Digestion Method 3052 was the method that will be used analyze the maximum metal concentrations in each cement product. The result will be compared to the Thai standards that are shown in the Table 1.3 to identify the cement as hazardous or non-hazardous.
9. ICP is the instrument that was used to analyze the components of heavy metals in the mixtures and clinker. Microwave digestion was used for changing the raw materials and samples from solid to liquid form before using ICP. 0.25 g of sample and clinker will be used.
10. Microwave digestion was the instrument use to analyze the leaching behavior and pH of the heavy metals in the cement products.
11. ASTM C109/C109M-05 was the method used to analyze the total maximum load and compressive strength value of the cement product. The test ages of the cement products will include 1 day, 7 days, and 28 days.
12. In each experiment, a blank was run before performing the other experiment.

Table 1.1: Concentrations of heavy metal in the kiln feed

Type of heavy metal	Literature (ppm)	Cement plant (ppm)	Concentration of heavy metal in experiment (ppm) (input)			
			1	2	3	4
Cr	50,000	SCCC 5,000 Other 5,000	5,000	10,000	25,000	50,000
Ni	20,000	SCCC 1,000 Other 10,000	1,000	5,000	10,000	15,000
Zn	25,000	SCCC 10,000	3,000	10,000	25,000	50,000

Table 1.2: Concentrations of metal oxide input in kiln feed samples.

Type of heavy metal	Concentration of metal oxides from the calculation for adding them into the kiln feed sample (g)			
	1	2	3	4
Cr ₂ O ₃	146.15	292.31	730.77	1,461.54
Ni ₂ O ₃	28.18	140.89	281.77	422.66
ZnO	37.34	124.47	311.17	622.34

Table 1.3: Limit of heavy metal concentrations from the Thai standards, 2005

Heavy metals	Limit concentration (ppm)
Chromium and/or chromium (III) compound	2,500
Chromium (VI) compound	500
Nickel and/or nickel compound	2,000
Zinc and/or zinc compound	5,000

Table 1.4: Physical and chemical analysis

Physical	Chemical
1. Total maximum load	1. Component of heavy metal
2. Compressive strength	2. Structure of clinker
	3. Leaching behavior in cement

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Chapter II

THEORITICAL BACKGROUND AND LITERATURE REVIEW

Theoretical background

'Ordinary Portland Cement' is the normal, grey, cement with which most people are familiar (Neville, 2003; Bensted and Barnes, 2002; and Mindess, Young, and Darwin, 2003). This type of cement is made by heating mixture of limestone and clay in kiln in a 1450°C. The resulting material is called clinker. Clinker is a nodular material before it is ground up. The nodules can be anything from 1mm to 25mm in diameter. The clinker is then ground into a fine powder and blended with a bit of gypsum to control the solidification time of the cement. Adding gypsums appropriately allows cement to gain its maximum strength.

2.1 Types of cement production processes

At this time, there are five cement production processes in use: the dry process, wet process, semi-dry process, pre-calciner kiln, and pre-heater kiln process. In Thailand, the wet and dry processes are popularly used for producing cement product.

2.1.1. Wet process: In this process, limestone and other raw material are wet and contain a 30-40% of moisture content. The mixture is fed into the cooler inlet of the kiln and flows down into the hot place at the end of kiln. The wet process uses longer period time than the dry process because a substantial portion of kiln length is used for the evaporation of slurry water. The wet process requires more energy to remove the moisture content in raw feed: around 1,523-1,668 Kcal/kg is used to produce clinker (US EPA, 2006). Moreover, in the wet process it is difficult to control the conditions for improving the quality of the cement and quantity of compounds in the raw materials.

2.1.2. Dry process: Dry raw materials such as limestone and raw material are feed into the inlet of the kiln. The meal flows down through the sloped kiln as it is thermally treated. Both the dry process and wet processes are similar in their operation, but dry process require a smaller diameter of kiln than wet process because no evaporation zone. In the dry process there is a high temperature of exit gas that flows out from the exit gas zone of around 450°C, so water sprays are used to cool the temperature of the exit gas before it flows out. Increased energy efficiency is a major advantage of the dry process in comparison to the wet process; the dry process has a 25% higher efficiency. Furthermore, the dry process uses energy only 1251-1390 Kcal/kg of energy (US EPA, 2006). However, the dry process is more complicated in operation than the wet process.

2.2 Steps of cement production

2.2.1. Raw material preparation: The properties of Portland cement investigated by mineral composition in the kiln feed or raw material. The concentrations of the minerals in Portland clinker are described in Table1 (Phillips and Muan, 1958; MAST modules; University of Illinois 1995; Bensted and Barnes, 2002).

Table 2.1: Chemical concentrations of minerals in clinker

Types of minerals	Chemical formation	Percent concentration in clinker
Alite	$3\text{CaO}\cdot\text{SiO}_2$	55-65%
Belite	$2\text{CaO}\cdot\text{SiO}_2$	15-25%
Aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	8-14%
Brownmillerite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	8-12%

Moreover, chemical oxides inside the clinker should make up 95% of clinker; these oxides come from the mineral or raw materials. The types of chemical oxides are described in Table 2.2:

Table 2.2: Concentrations of chemical oxide in clinker

Types of chemical oxide	Concentration inside clinker
CaO	55-65%
SiO ₂	18-22%
Al ₂ O ₃	4-6%
Fe ₂ O ₃	2-4%

The lime saturation factor (LSF), silica ratio and alumina ratio were other important value of clinker material. These ratios calculated from formula (Bensted and Barnes, 2002):

$$\text{Lime saturation factor} = \text{LSF} = 100(\text{CaO} + 0.75\text{Mg}) / (2.85\text{SiO}_2) + (1.18\text{Al}_2\text{O}_3) + (0.65\text{Fe}_2\text{O}_3)$$

For MgO below 2%

$$\text{Lime saturation factor} = \text{LSF} = 100(\text{CaO} + 1.5\text{Mg}) / (2.85\text{SiO}_2) + (1.18\text{Al}_2\text{O}_3) + (0.65\text{Fe}_2\text{O}_3)$$

For MgO above 2%

$$\text{Si ratio} = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$$

$$\text{Al ratio} = \text{Al}_2\text{O}_3 / \text{Fe}_2\text{O}_3$$

The lime saturation factor controls the potential C₃S to C₂S ratio in the finished cement. C₃S governs the early age strength development while C₂S governs the later age strength. The alumina-to-iron ratio is important because it controls the potential

C₃A/C₄AF ratio in the finished cement, which is important because of sulfate resistance, heat generation, and admixture compatibility issues. The silica ratio represents the burnability of a raw mix. The burnability impacts how much energy is put into the system. As the ratio of silica to alumina plus iron increases, it becomes harder to “burn” — harder to combine the raw materials into the phases we want

2.2.2. Raw material crushing: Single or twin rotor hammer crushers and impact crushers are used for primary size reduction. At this time, the rotor hammer and impact crusher are used to increase the maximum feed size and raise the maximum feed moisture content of the raw material. At present, the twin-rotor hammer crusher can permit moisture content in the raw material of 10 to 20% and the individual lump of feed materials has increased to 7 tonnes (Bensted and Barnes, 2002).

2.2.3. Raw material grinding: Both the dry and wet processes use ball mills for grinding the raw materials. The difference is that the dry utilize an air classifier, while the wet process operates in a closed system inside a vibrated screen or arc-screen . The energy consumption in the ball mills is heavily influenced by the grinding media filling ration, design of the mills liners, and grinding media in the last chamber. The main point of the grinding process is to make sure the raw materials are in a suitable granulated form.

2.2.4. Classification: Classifiers are very important for mill efficiency and consequently on energy consumption. The energy consumption of classifiers is 35 kWh/t for 100 percent classifier efficiency. This can be compared with the energy consumption of the ball mill grinding that uses 65 kWh/t (Bensted and Barnes, 2002). At this time, there are two kinds of popular classifiers in cement plants: grit separators and mechanical separators.

2.2.5. Raw material burning: The raw materials are added and heated inside a cement kiln. The cement kiln is a slowly rotated and sloped cylinder. The temperature increases to a peak of temperature of around 1400-1450°C. During this process, if the temperature too low in this operation, incomplete combustion will occur and the clinker will not set properly (Neville, 2003; Bensted and Barnes, 2002; and Mindess, Young, and Darwin, 2003). On the other hand, if the temperature is too high, the mass or glass will melt and destruct the cement kiln. When the temperature increases to 1400-1450°C, the raw materials are melt and change to a liquid from like lava. The result from this process is called clinker. A 5% quantity of gypsum is added to the clinker and then mixture is grind in ball mills to form of cement powder. Cement powder is kept in silos for around 1-20 weeks depending upon the local demand (Neville, 2003; Bensted and Barnes, 2002; and Mindess, Young, and Darwin, 2003). Figure1 summarizes the step of Portland cement production process.

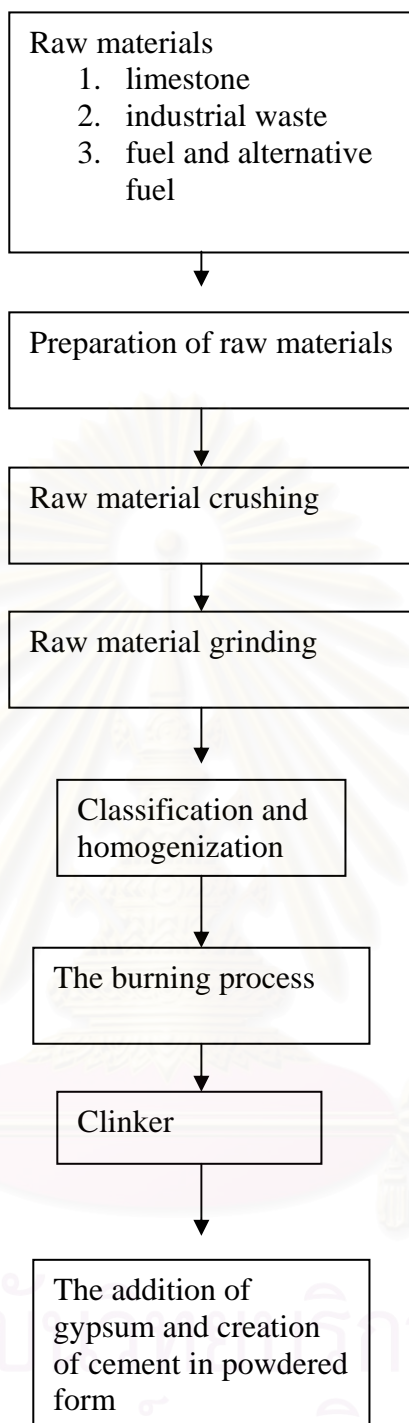


Figure 2.1: Steps of the Portland cement production process

2.3 Chemical composition in Portland cement

2.3.1 Calcium silicates (C_xS_y) are found in four binary phases within the system, which becomes increasingly hydraulic with an increasing C/S-ratio. C_3S (alite) and C_2S are mainly found in Portland cement (Welch and Gutt, 1959).

2.3.1.1 C_3S (alite) is a highly hydraulic compound; 50-90% of Portland cement is made up of this compound. It is formed above 1250°C from the reaction of C_2S and C. It is not stable when the mixture is rapidly cooling. 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°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).

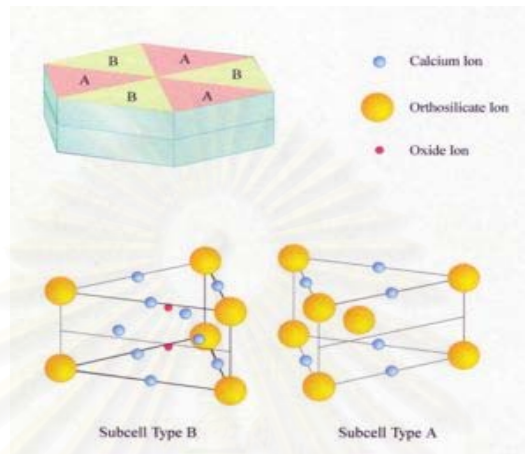


Figure 2.2: Structure of alite

2.3.1.2 C_2S (belite) is present in Portland cement at around 10-40%. C_2S can be found in several phases of transformation according to the range of the temperature. 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):

2.3.1.2.1 Primary belite is formed by reactions between the lime and silicon sources.

2.3.1.2.2 Secondary belite is formed by the decomposition reaction of 'alite'
 $\text{C}_3\text{S} \rightarrow \text{C}_2\text{S} + \text{C}$: this reaction forms small crystals on the rims of alite crystals.

2.3.1.2.3 Tertiary belite is due to the recrystallization of the interstitial phase coming from the decomposition and decreased solid solution of SiO_2 in the C_3A -phase.

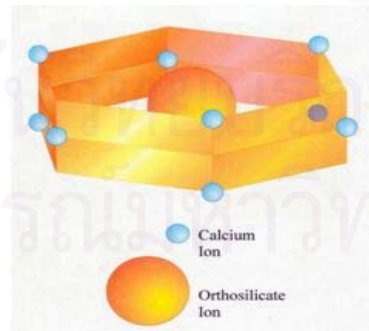


Figure 2.3: Structure of belite

2.3.2. Tricalcium Aluminate is the most abundant Al contained in Portland cement, but CA is the most important in high alumina 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 in a cubic form, but it incorporates with alkalis (Na replace to Ca), and SiO_2 , and changes to the

orthorhombic and monoclinic forms. The ranges of the Na ion can change C₃A form as follow (Bensted and Barnes, 2002):

- 0-1.9% Na₂O = cubic form
- 1.9%-3.7% Na₂O = cubic + orthorhombic
- 3.7%-4.6% Na₂O = orthorhombic
- 4.6%-5.9% Na₂O = monoclinic

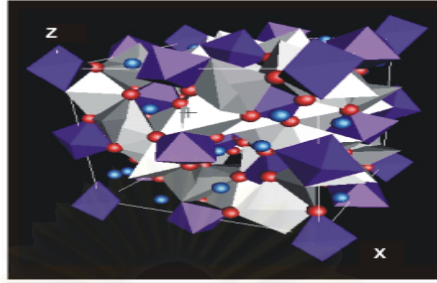


Figure 2.4: Structure of Tricalcium Aluminate

2.3.3 Calcium aluminium ferrite is an iron that is mainly fixed under the oxidizing condition in the calcium aluminate ferrite phase. The composition of the ferrite phase can be described by the limited of solid solution between C₂F and C₆A₂F. In nature, this mineral is named “brownmillerite”(Bensted and Barnes, 2002, and Mindess, Young, and Darwin 2003). In typical clinkers, the uptake of magnesium, titanium, and silicon takes place and can be given by following equation:

$2\text{Fe}^{3+} \longrightarrow (\text{Si}^{4+} + \text{Ti}^{4+}) + \text{Mg}^{2+}$. Fe dictates the burning condition. Reducing the condition can lead to the formation of Fe²⁺. It leads to the increased formation of calcium aluminate and free lime. Fe²⁺ cannot be incorporated in the ferrate phase.



Figure 2.5: Photomicrograph of clinker (0.11mm.) that contain alite (blue), belite (orange), tricalcium aluminium (grey), and ferrite (white).

2.4 Simple elements and oxides in the cement phase

Cement’s chemistry is dominated by its free lime contents, which are measured in cement plants for quality control. High free limes contents can be indicate that the burning condition or homogenizations have not successfully adapted. Low-burnt clinker can increase free lime contents. Free lime and free magnesia contents in clinker are restricted due to the hydration of on-expansion reactions which can occur

in the final product. SiO_2 come from coarse quartz in the raw meal or incomplete homogenization. Iron oxide can occur in the reduction condition of the clinker process. The incorporation of Fe^{2+} in alite can lead to a destabilization of alite (Mindess, Young, and Darwin 2003).

2.5 Heavy metals in cement

2.5.1. Chromium

Chromium is a heavy metal that can found naturally in rocks, soil, and plants. Chromium cannot evaporate but it can appear in air in form of particle. In nature, chromium can found in three forms: metal ore, trivalent chromium Cr (III), and hexavalent chromium Cr (VI). Chromium is regarded as a human carcinogen. 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 milligrams per liter (Diane et al, 1992). So, Cr (VI) is strongly regulated, and a reducing agent such as Fe^{2+} salt is sometimes added during cement production (Bensted and Barnes, 2002; and Pollmann et al, 1997). In cement industries, chromium is found in limestone, clay, char, and oil, which are the fuel sources used in production processes (Sprung, 1985). In addition, Chromium can in the form of contamination from abrasive wear that happens in the cast iron balls during the milling of raw meal in the ball mill (Barros, 2004). The use of bauxite as a source of alumina may increase concentration of chromium on the final product (Barros, 2004). Chromium has been found in industrial hazardous waste in the following concentration: 737 mg/l in burnt used oil (Trezza and Scian, 2000), 0.14% in galvanic sludge from electroplating factory (Espinosa, 2003), and 41,700 mg/L in sludge from a metal plate factory. In the hydration of cement, chromium can incorporate in ettringite. At pH 11-13, the sediment of $\text{Cr}(\text{OH})_3$ was found and solution is Cr(VI). At pH 9-13, Cr(III) and Cr(VI) are incorporated into ettringite and contain in calcium sulphoaluminate hydrate(Aft and AFm phase) (Gouger, Scheetz, and Roy, 1996). At pH lower than 3, Cr exists as CrOH^{2+} .

2.5.2 Nickel

Nickel is a heavy metal that can found in the nature such as in soil and volcanoes. Pure nickel is hard, and silver-white in color. Nickel is mixed 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. Ni is extremely toxic when its form in $\text{Ni}(\text{CO})_4$ 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 the production of Portland cement are similar to chromium. 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 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 $\text{Ni}(\text{OH})_2$ and stable. In a CSH product, $\text{Ni}(\text{OH})_2$ is incorporated or sorpted. At pH lower than 8, nickel leaches rapidly and in the form of Ni^{2+} (Gougar, Scheetz, and Roy, 1996).

2.5.3 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 is present as a minor element in tires (Andrade, Maringolo, and Kihara 2002). Zinc has been found in hazardous waste at the following concentration: 114,483 mg/l in burning used oil (Trezza and Scian, 2000), and 227,000mg/l in sludge from metal plate factories. 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 $\text{Zn}(\text{OH})_2$. 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°C . Up to 4.7 % of zinc can stabilize different polytypes of C_3S (Odler, 1990). Other phase with Zn was described- $\text{Ca}_2\text{ZnSiO}_5$ and different calcium aluminum zinc oxides are other phases that have been found with Zn. ZnCO_3 appears at pH 7-8.

2.6 Basic instrument for analyzing cement

2.6.1 XRF

XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials. When materials are exposed to short wavelength x-ray or gamma-rays, ionization of their component atom may take place. The term fluorescence is applied to phenomena in which the absorption of higher-energy radiation results in the re-emission of lower-energy radiation. The removal of inner electron by energetic photon cause of outer electron is take place. The transition yield is important for calculated a fluorescence radiation. The result can find from main transitions line included: an $\text{L}\rightarrow\text{K}$ transition is traditionally called $\text{K}\alpha$, an $\text{M}\rightarrow\text{K}$ transition is called $\text{K}\beta$, and an $\text{M}\rightarrow\text{L}$ transition is called $\text{L}\alpha$ (Beckhoff, B.2006). The sample of electron transition was shown on figure. The table 2.5 showed the line and wavelength of element, which measured by XRF and the example of heavy metal was showed on figure.

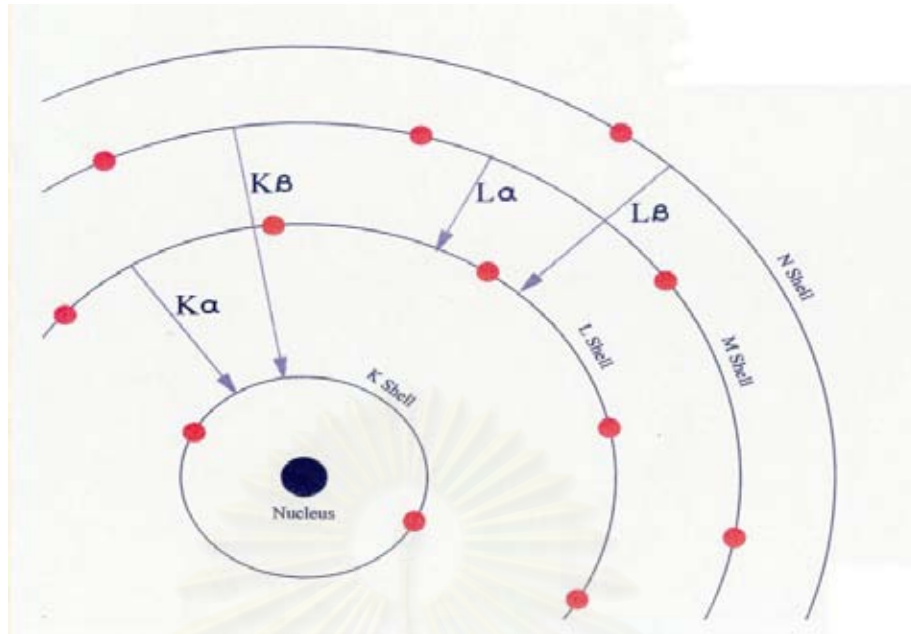


Figure 2.6: Electronic transitions in a calcium atom

Table 2.3: The types of element can measure from line, and each wavelength as follow (Beckhoff, B.2006):

Element	Line	Wavelength (nm)
Mg	$K\alpha_{1,2}$	0.989
Si	$K\alpha_{1,2}$	0.7126
Al	$K\alpha_{1,2}$	0.834
Ca	$K\alpha_{1,2}$	0.3359
Ni	$K\alpha_1$	0.1658
Cr	$K\alpha_1$	0.2290
Zn	$K\alpha_1$	0.1435
Cd	$K\alpha_1$	

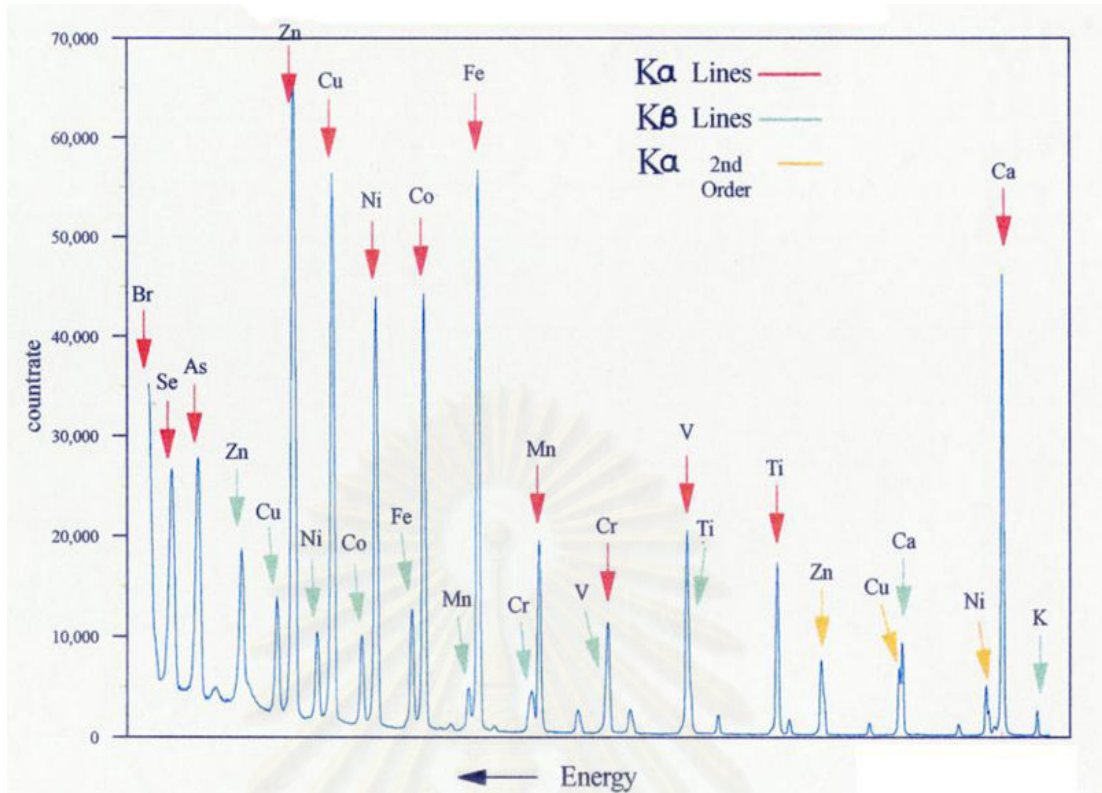


Figure 2.7: The example of heavy metal line that analyzed by XRF

2.6.2 XRD

XRD is the one of the most important techniques for analyzing crystalline component in the cement phase (Bensted and Barnes, 2002). This instrument finds the material inside cement phase but if the correct experimental techniques are used, XRD can give a semi-quantitative or quantitative analysis of component in the crystalline fraction (Taylor and Aldridge, 1994). The material was changed into powder mixture form before analyze component. The powder sample was pressed into a sample holder and must have a smooth flat surface. The correct value can changed due to the reflection of x-ray to the rough surface of sample (Taylor and Aldridge, 1994, and Bensted and Barnes, 2002). The example of XRD analysis was shown on the figure 2.8.

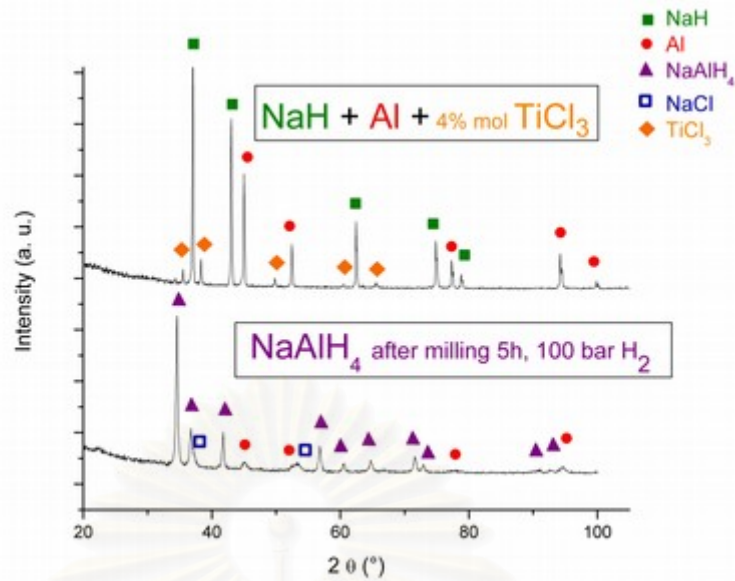


Figure 2.8: XRD analysis of NaH + Al + 4% mol of TiCl_3 and NaAlH_4 after milling 5h, 100 bar H_2

The quality of any XRD pattern will depend on (Bensted and Barnes, 2002):

- 1.1 the alignment of the diffractometer
- 1.2 the choice of the diffraction condition included time, slits, monochromator, and filter
- 1.3 the sample preparation physical factors

2.6.3 SEM

SEM-EDX is one types of SEM which use energy dispersive X-ray spectrometer to enable the chemical analysis of bulk specimens. The process of this instrument is the X-ray generate in specimen is $1\text{-}2\mu\text{m}^3$ compositional analyses of hardened cement very often correspond to mixture of phase (Bensted and Barnes, 2002). A flat, polished surface of sample is very important for quantitative analysis. The reason is surface can affect to the matrix correction factor. Analysis of proportion of elements in sample, the number of characteristic X-ray counts for each element in specimen must be compared under identical condition with those arriving from standards of known composition. As specimens differ from each standards in its density and average atomic weight, several matrix correction procedure need to be applied to obtain more accurate compositions. After polishing, a conducting paint should be applied around the edge of the specimens followed by the evaporation of carbon onto surface. Carbon is used because of its low atomic number, ensuring minimum absorption on the emerging X-rays. Another type of SEM which using X-rays is wavelength dispersive spectrometers (WDS). EDX and WD can be both to use for analyzing distribution of element in a sample. The different between two types is EDX is easily achieved by scanning the beam over the area of interest but in WDS, the specimens must be mechanically moved under the beam to maintain the spectrometer focusing condition.

Literature Review

The burning of the hazardous waste in rotary cement kilns for producing clinker is the one method for reducing the concentration of hazardous waste.

2.7 Pilot- scale rotary kiln parts

Lemieux et al. (2005) tested dibenzo-*p*-dioxin and polychlorinated dibenzofurans from carpet waste by burning the waste in a pilot-scale rotary kiln incinerator. Testing was performed in a pilot-scale rotary kiln incinerator to evaluate the potential for formation of PCDDs/Fs (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) from the combustion of carpet. The production process was performed at the EPA's Rotary Kiln Incinerator Simulator (RKIS). The incinerator was consisted of a 73 kW (250,000 Btu/hr) natural gas-fired rotary cement kiln section and 73 kW natural gas-fired secondary combustion chamber. Following the secondary combustion chamber is a long duct that leads into dedicated flue gas chamber system, which included another afterburner, baghouse, and wet scrubber. Thermocouples were used to monitor the temperature throughout the system. The temperature in the transfer duct was maintain at approximately 300-350°C. Five runs were performed at three test conditions (combustion blank, carpet wetted with deionized water, and carpet wetted with a 10% bleach solution or sodium hypochlorite). They found the combustion blank produced extremely low emission of PCDDs/Fs and chlorinated species. Emissions of PCDDs/Fs from the carpet wetted with deionized water were somewhat higher those of the combustion blank, but were still low. But the condition with the deionized water showed an increase in some species, particularly 2, 3, 7, 8- TCDF and the 2, 3, 4, 7, 8-PeCDF isomers. The homologue distribution for the tested condition with bleach solution was flat, and the contribution of the octa-chlorinated species was significant. They concluded that carpet that was contaminated with a chlorinated agent such as bleach may require care to prevent an increase in PCDD/F emissions.

Louisiana State University (2003) established a rotary kiln incinerator for testing and destroying hazardous wastes in the forms of food, clothing, and shelter. The indicators included CO, CO₂, HCl, NO_x, and SO_x. The component of incinerator included the following: 1) batch feeder was a water-cooled, pneumatically driven ram with an 8" diameter by 20" long compartment for injecting containers of waste. 2) rotary kiln, as the primary oxidation chamber, was a refractory-brick-lined, horizontal, steel drum, mounted on a roller. The inside diameter was 31" and the length was 90". The kiln was rotated by a ½ horsepower, and used 1.2 MM Btu/hr of natural gas and a temperature around 1800°F. 3) afterburner, the secondary oxidation chamber, was a refractory -brick – lined vertical, stationary steel furnace that supported a rotary kiln. In this place, auxiliary burner was used energy 1.2 MM Btu/hr to heat the incoming gases from the kiln and increase to temperature around of 2200°F. 4) boiler was a fire-tube boiler that generated 10 psig for cooling the hot gases from the afterburner. The gases entered the tubes at 1800°F and were cooled to about 275°F. The cooling was necessary to prevent damage to the filter bag in the next stage. 5) baghouse was the filter used that contain 25 bags with a total area of 250 square feet. The particulate matter or soot formed a cake like layer in this place. 6) scrubber was a packed tower in which the gases exiting the baghouse flow countercurrent to a weak caustic solution to remove acids or residual particulates. 7) induced draft fan drew the

combustion gas from the scrubber and all of the upstream equipment, maintaining a vacuum so that gases could not leak from the upstream components. 8) The exhaust stack had an internal diameter of 10 inches and a height of 30 feet tall. It was lined with refractory gunite. If the process was fault the damper in stack operated automatically to change the flow from the afterburner directly to the stack. The location of the rotary kiln incinerator was 1500 square feet in open steel structure, and small building was used as the control room.

Rehmet et al (1999). produced cement from sediment in New York/New Jersey harbor by Cement-Lock Technology. The Cement-Lock Technology is an advanced management system for remediating contaminated dredged sediments from estuarine and river environments, hazardous and nonhazardous wastes, and municipal solid wastes (MSW). Conventional MSW incinerators do not produce a salable product. Rather, they generate ash that may contain leachable heavy metals, which must be disposed of as hazardous waste. Furthermore, MSW incinerators have been shown to generate dioxins and dioxin precursors. The rotary kiln melter for the demonstration-scale project was ordered from Andersen 2000 (Peachtree City, Georgia). The melter was 10 feet in diameter and 30 feet long. The entire system consisted of a raw sediment storage bunker, hoppers for modifiers, screw conveyors for moving material to the melter, a pug mill for blending all of the feed materials before charging, the rotary kiln melter, a quench/granulator, a secondary combustion chamber, a flue gas quench system, a lime injection, a bag house, and an activated carbon adsorption system. The result from experiment was hazardous organic contaminants from estuaries (PCBs, PAHs, grease, dioxin) were destroyed and the values of them were lower than standard limits in USA.

2.8 Physical and chemical properties of the heavy metals in the cement phase

Many types of hazardous or non-hazardous waste contain heavy metals. Heavy metal can change the characteristic of the cement. They can improve or reduce the quality of the cement structure, and have been the topic of research.

Andrade et al. (2002) studied how V, Zn, and Pb were able to be incorporated in Portland clinker. These three types of heavy metals can found in the alternative fuel petcoke (V) and industrial waste such as fuel and industrial waste (Pb), and used tires (Zn). In the experiment, one blank control and three series with the addition of 1 wt% of NH_4VO_3 , ZnO, and $\text{Pb}(\text{NO})_3$ were set. The blank sample and mixture samples were pre-heated at 100°C for 12hr and then burned in a muffle furnace. XRF analyzed the concentrations of the compounds in cement clinker and mixture samples. Electron microprobe and scanning electron microscope were used for analyzing the structure of the cement. The result showed that in the burning process, Cr, Ni, and Zn could affect the burning ability and reactivity of the major phase of clinker. The burning ability increased if the metal concentration of these three heavy metals increased (2.5-5.0 wt%). In the cement phase analysis, 86.6% Zn, 69.9% V, and 37.1% Pb were incorporated in the cement phase. Zn appeared in higher amounts in periclase (MgO), and C_3S had a higher Zn content than C_2S . Pb concentrates in minute spherules and partitions toward C_3S in small amount. The recognition that V, Zn, and Pb are retained in the crystal structure of the clinker phase, mostly as a solid solution, was a favorable environmental aspect. V was in the C_2S phase.

Stephan et al. (1999) produced cement from three types of heavy metals (Cr, Ni, and Zn) by burning them in an electrical heat furnace. The phases of the clinker were analyzed by light microscopy and scanning electron microscopy (SEM). These samples were also analyzed by means of X-ray powder diffraction (XRD). After the dissolution of the samples in a mixture of nitric acid, hydrofluoric acid, and boric acid, the heavy metals content were analyzed by means of graphite furnace atomic absorption spectrometry (AAS). The strength development of cement is one of the most important properties for practical use; therefore, the strength development of the cements was tested. Test specimens (1.5·1.5·6.0 cm) of mortars with a water/cement ratio of 0.32 and an aggregate/cement ratio of 1 were produced from all cements with 5,000 and 25,000 ppm of heavy metal. From their results, they concluded that the heavy metals Cr, Zn, and Ni had no influence on the formation of the cement clinker phase during the burning process at concentration that are normally present in clinker. Moreover, at the concentrations which 10 and 20 times higher there were no changes. However, very high intakes of Cr, Ni, and Zn caused changes. Up to 0.5 wt.% Cr lowered the content of free lime in the clinker, but 2.5 wt.% led to the decomposition of the alite and, consequently, to more belite and free lime. Cr was mainly found in the belite, but if the concentration of K was high enough in the clinker, K_2CrO_4 and/or $K_2Cr_2O_7$ is formed also. Very high concentration of Ni affected only the content of free lime as well as the content on the phase. In clinkers with higher concentrations of Mg, a new compound $MgNiO_2$ had been detected. Zn also had a small influence on the content of free lime. The heavy metals Cr, Ni, and Zn have no influence on the strength of the cement mortar, and the initial setting at concentrations that are normally present and 10 to 20 times higher in the clinker. However, very high concentrations of the heavy metals Cr, Ni, and Zn caused changes in the hydration properties. High concentrations of Cr result in a lower strength level than the one present in the controlled sample. Ni has very little influence on the hydration of the cement. The strength of the mortars with Ni was equal to or higher than that of the control. Zn had a strong retardation effect on the hydration of cement and also led to a retardation of the initial setting. In most cases, the strength of mortars with Zn was higher than that of the control.

Galvanic sludge is the one of the main types of hazardous waste from industry. This waste is contains a lot of heavy metals, especially chromium, which is a heavy metal that causes cancer and skin eczema problems into humans. Nickel is also found in galvanic sludge. So, some researches studies analyzed the characteristics of heavy metals in galvanic sludge.

Espinosa et al (2003). studied galvanic sludge's influence on the clinkerization process. The galvanic sludge was obtained from the chromium electroplating process. The sample test included raw materials and a mixture of raw material and dry sludge. These mixtures contained 0.25, 0.5, 1.0, 2.0, 3.0, 5.0 and 8.0 wt. % of dry sludge. The sludge was dried at 60°C and previously milled. The mixtures were prepared by adding the galvanic sludge to the cement raw meal, and afterwards those mixtures were homogenized in a rotating cylinder for 2 h. Then, the mixtures were maintained in an oven at 60°C in order to avoid water absorption. After that, the mixture samples were burnt in a furnace. XRD and XRF measured the concentration of elements and compounds in the raw material and mixing samples. 21.0 ppm of Cr, 57.7 ppm of Ni, and 41.7 ppm of Zn were contained in the raw material, while, 39,000 ppm of Cr, 300 ppm of Zn, 46.2 ppm of Ni were contained in

the chromium electroplate. DTA tests were performed to verify the effects of the sludge additions on the reaction temperatures during clinker formation. These experiments demonstrated that the addition of up to 2 wt% of galvanic sludge did not have an effect on the clinker reaction. During the burning process, Cr emission was less than 0.1%, so Cr retention was 99%. Moreover, the incorporated Cr was not released during leaching and solubilization tests. It remained trapped in the clinker. The leaching tests were performed according to Brazilian Standards (NBR, 1987a) 10.005 17, similar to EPA acetic acid leaching test). In their results Cr^{6+} and total chromium were lower than the standard (5 mg/L). In addition, Cr saturation was not observed for the studied galvanic sludge additions (up to 3 wt. %). At the 8 wt% of the mixing sample, the material product contained a lot of sodium and potassium chloride.

They also studied into determining the of Cu and Ni incorporation ratios in Portland cement clinker in year 2003. Cu and Ni are usually found in galvanic sludge, a hazardous waste. So, this study was concern with the co-incineration of galvanic sludge containing Cu and Ni along with Portland cement clinker. The galvanic sludge came from a local company. Atomic absorption spectrometry chemical analysis, differential thermal analysis (DTA), thermogravimetric analysis (TG) and XRF were utilized. Leaching tests verified Cu and Ni incorporation into the clinker structure. The leaching test was performed maintaining 100 gof broken briquettes in 1600 ml of deionized water; this solution was agitated during the entire test. 0.25, 0.5, 1.0, 2.0, 3.0 and 5 wt.% were the percent mixture of galvanic sludge in sample. The results from this study showed that all Ni and over 99 wt.% of Cu were incorporated into the clinker during the burning process and additions of up to 2 wt.% of a galvanic sludge containing 2.4 wt.% Cu and 1.2 wt.% Ni to clinker raw-material was not affect the clinkering reactions.

Used oil from cars is the one type of raw material, which is used in cement plants, Zn and Cr can found in the oil. Some researcher studied the effects of used oil into the cement phase.

M.A. Trezza and A.N.Scian (2000) looked into the effects of alternative fuel on cement clinker. Ash from used oil was the raw material. XRD analyzed the elements in the clinker, while, DTA measured the effect of temperature on clinker. Strength was also tested at 1hr, and 1, 7, and 28 days. 0, 0.005, 0.01, 0.02, and 0.04 % w/w of ash were added into the raw material. Clinker furnaces were used for the burning process. The DTA recorded 20-1450°C the temperatures that had increased at 10°C/min, the temperature reached it peak at 30 min at 1450°C. When the temperature cooled down from 1450-1350°C is reduce 40°C/min. Increase addition of ash into raw material caused of reduce energy in burning process. The mechanical strength at 3 and 28 days of paste the prepared paste with w/c= 0.4 at 0.04% of ash in mixing sample produce higher strength performance than the blank.

Disposing of hazardous waste (called co-processing) is a new technology based on waste-derived and alternative fuels. This method converts waste into raw materials or fuel for cement production process. The destruction of hazardous waste also occurs. Taweekitwanit (2004) studied the leaching behavior of chromium, zinc, and nickel that occur while using this method. Cement clinker is produced by a static system. To study of leaching behavior, Microwave-assisted leach method 3051A,

availability leaching test (NEN 7341), and pH static leach test were used. The results showed that more than 80% of chromium and zinc were likely to be leached from the cement into the environment, while 3% of nickel was leached. From the pH static leach test, chromium was effectively leached at the pH range of 4-10. Zinc and nickel were effectively leached at pH 4 but the ability of leaching in zinc and nickel decreased when pH increased. The toxicity characteristic leaching procedure (TCLP) and 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 material was doped with more than 0.1 wt% of chromium, the cement was classified as hazardous waste. On the other hand, the raw material that had been doped with up to 2 wt% of nickel and zinc was not classified as hazardous waste.

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 2.4 lists the standard limit of several countries (Holcim, 2006).

Table 2.4: 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	-

In Germany, standard concentrations of heavy metals in raw meal, clinker, and Portland cement were published in year 2000 by the German cement industry called the VDZ. These values are shown in Table 2.5.

Table 2.5: Maximum, minimum, and average concentration of heavy metals in raw meal, clinker, and Portland cement published by the VDZ in the year 2000

Material		Cr (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)
Raw meal	Min	23	5	12	10
	Max	59	19	38	108
	Average	30	14	20	34
Clinker	Min	10	5	10	29
	Max	422	136	397	600
	average	66	38	38	113
Portland cement	Min	25	14	14	21
	Max	712	98	97	679
	average	68	33	45	164

In Thailand, heavy metals concentrations in cement are investigated every month. Concentrations of heavy metals in cement from the SCCC follow the New Holcim guideline in for the year 2007. Table 2.6 and Table 2.7 reported on the heavy metals in cement from the market in May 2007.

Table 2.6: 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 2.7: 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 patch (plant3) [†]	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

[†] from 2 samples

The table 2.8 reported on the maximum concentration of heavy metals in waste was set by SCCC.

Table 2.8: Maximum concentration of heavy metal in waste was set by SCCC (Siam City Cement Co.)

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

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Chapter III

METHODOLOGY

3.1 Raw materials

As many as 118 bags of kiln feed, 10-15 kg in each bag, were sample and collected from the Siam City Cement Public Company Limited in Saraburi. Three types of metal oxides including ZnO, Ni₂O₃, and Cr₂O₃ were brought from Science Integration Company Limited. The blank material (the kiln feed without metal addition) and the different ratio of metals oxides were mixed with raw meal (called the mixture).

3.2 Pilot-scale rotary cement kiln

A pilot-scale rotary cement kiln was designed by the research team and constructed the Siam City Cement Public Company Limited. The parts of pilot-scale rotary cement kiln consist of a 1-meter- long rotary cement kiln with 15 mm. kiln shell thickness, and a cooling tower. The pilot-scale rotary cement kiln, driven by two horsepower of motor, rotates at 0.5 rpm. Inner kiln wall was casted with special C60 heat resistant cement to protect the extreme heat. A proper mixture of natural gas and air was controlled and feed into the burner. A stainless steel capsule was used as a tool to feed the mixture into the pilot- scale rotary cement kiln.



Figure 3.1: Pilot- scale rotary cement kiln



Figure 3.2: Stainless capsule for adding kiln feed

3.3 Sample preparation

Due to the fact that sample taken at different time possess different values of LSF of raw meal or kiln feed. High LSF value causes incomplete burning process, whereas low LSF value makes the liquid molten samples penetrated into and destroyed the protective concrete layer. In real operation, coal is used for primary fuel. The ash from coal is assimilated into clinker, thus, reducing LSF value to get complete formation of clinker. In the experiments, LPG was used as fuel, but there was no ash produced from the combustion to reduce LSF value. High silica also causes incomplete burning process. From this experiment, LSF value of kiln feed must be around 95 ± 1 whereas silica content of kiln feed must not be more than 2.6%. One hundred gram of kiln feed each from 118 bags were mixed to get around 10 kg of mixed kiln feed in the new bags. Then, the 10 kg of new kiln feed was mixed again in the mixing machine to obtain homogeneity. One kg of new kiln feed was added with 2.5% of mixing between shale core and clay to reduce LSF and silica value in the kiln feed. Then, the new mixtures were thoroughly mixed in a V-mixer to obtain homogeneity, and analyzed for LSF and silica ratio. If the determined value were acceptable, the metal oxides were added the mixtures and blend in the V-mixer machine again.



Figure 3.3: Mixing machine



Figure 3.4: V-mix machine



Figure 3.5: Collected kiln feed



Figure 3.6: New mixture between mixed kiln feed and 2.5% of mixed shale core and clay

3.4 Clinker

The raw meal was mixed with different ratios of metals oxides. Then, the mixed samples were roasted in an oven at 100°C for 12 hr. Next, the mixed samples were

brought into the pilot-scale rotary cement kiln and pre heated at 700-900°C for 10 minutes. Finally, the mixed samples were heated at 1450°C for 15-30 minutes for clinker to form. Figure 18 and 19 describe the steps for producing clinker

3.5 Analysis of Loss of Weight on Ignition and Moisture Content

The raw meal and clinker samples with and without mixing heavy metals will be analyzed for loss on ignition (LOI) and moisture content to get information on the quantity of carbon and the humid. The loss on ignition of cement clinker is generally not more than 3% (Thai Industrial Standard Institute, 2002). The LOI process includes the following steps:

3.5.1 Weigh the crucible dish or cup and tare the scale to set a 0 point.

3.5.2 Weigh the raw mill or clinker.

3.5.3 Roast the sample at 105°C for 24 hr.

3.5.4 Calculate the percentage of moisture content by formula

$$\text{Percent of moisture content} = \frac{(\text{initial conc.} - \text{conc. after roasting})}{\text{initial conc.}} \times 100$$

3.5.5 Bring the sample into the bomb calorimetric machine for desiccating and setting the sample at 700-900°C for 30 min.

3.5.6 Calculate the LOI using the following formula

$$\text{LOI} = \frac{(\text{conc. after roasting} - \text{conc. after desiccation})}{\text{initial conc. before roasting}} \times 100$$

3.6 Analysis of the Structure and Chemical Properties of Samples by XRD, XRF, and SEM

The Clinker sample around 50 g was ground by a swinging mill to reduce the size of clinker in 30s. Then, around 20 g of clinker sample was milled by swinging mill again at 30s for analysis of free lime. Another 20 g of clinker sample was added with bromine for trapping the clinker and milled for three minutes for analyzing total concentration of chemical inside clinker. XRF used for analyzing chemical oxide whereas XRD was used for analyzing free lime and chemical mineral. SEM was used for analyzing particle morphology by cutting the surface of clinker.

3.7 Analysis of 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 will be maintained at 23±3.0°C (room temperature). The humidity should not be less than 50%. The clinker samples will be grinded by a ball mill and mixed with 5% per weight of gypsum to control the solidification time of cement. The quantities of materials to be mixed at one time in a mortar for making six test specimens shall be as shown (ASTM C109/C109M-05, 2005) in Table 3.1:

Table 3.1: Properties of 6 g of cement for testing strength of cement sample

Cement	500 g
Sand	1375 g
Water	242 ml
water-cement ratio	0.485

The cubic shape of cement samples will be tested on 1 day, 3 days, 7 days, and 28 days All test specimens for a given test age shall be broken within the permissible tolerance prescribed as follows (ASTM C109/C109M-05, 2005):

Test Age	Permissible Tolerance
24 hours	$\pm 1/2$ hour
3 days	± 1 hour
7 days	± 3 hours
28 days	± 12 hours

The compressive strengths of the samples were tested using a compressive machine and the results were compared against the standards of the Thai Industrial Standard Institute (2002) as shown in Table 3.2:

Table 3.2: Least compressive strength in specific ages

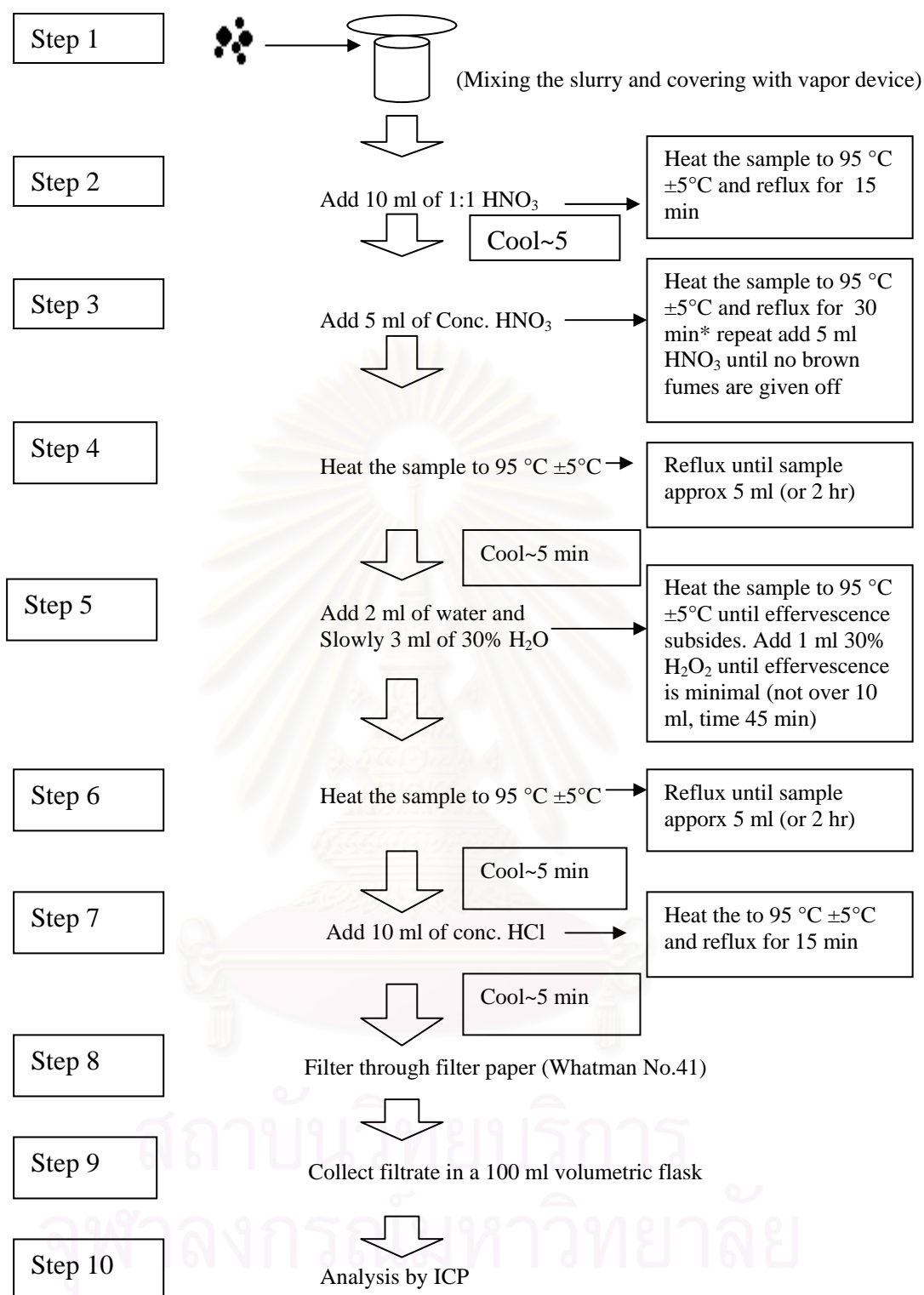
Time(day)	Least compressive strength value (kg/cm ²)
7	150
28	245

3.8 Analysis of Total Heavy Metals by Microwave Digestion Method 3050 B

This method utilizes a microwave digester for digesting the compounds that contain silica and organic compounds for analyzing total heavy metal in the sample. The details of the methods are described on figure 3.7.

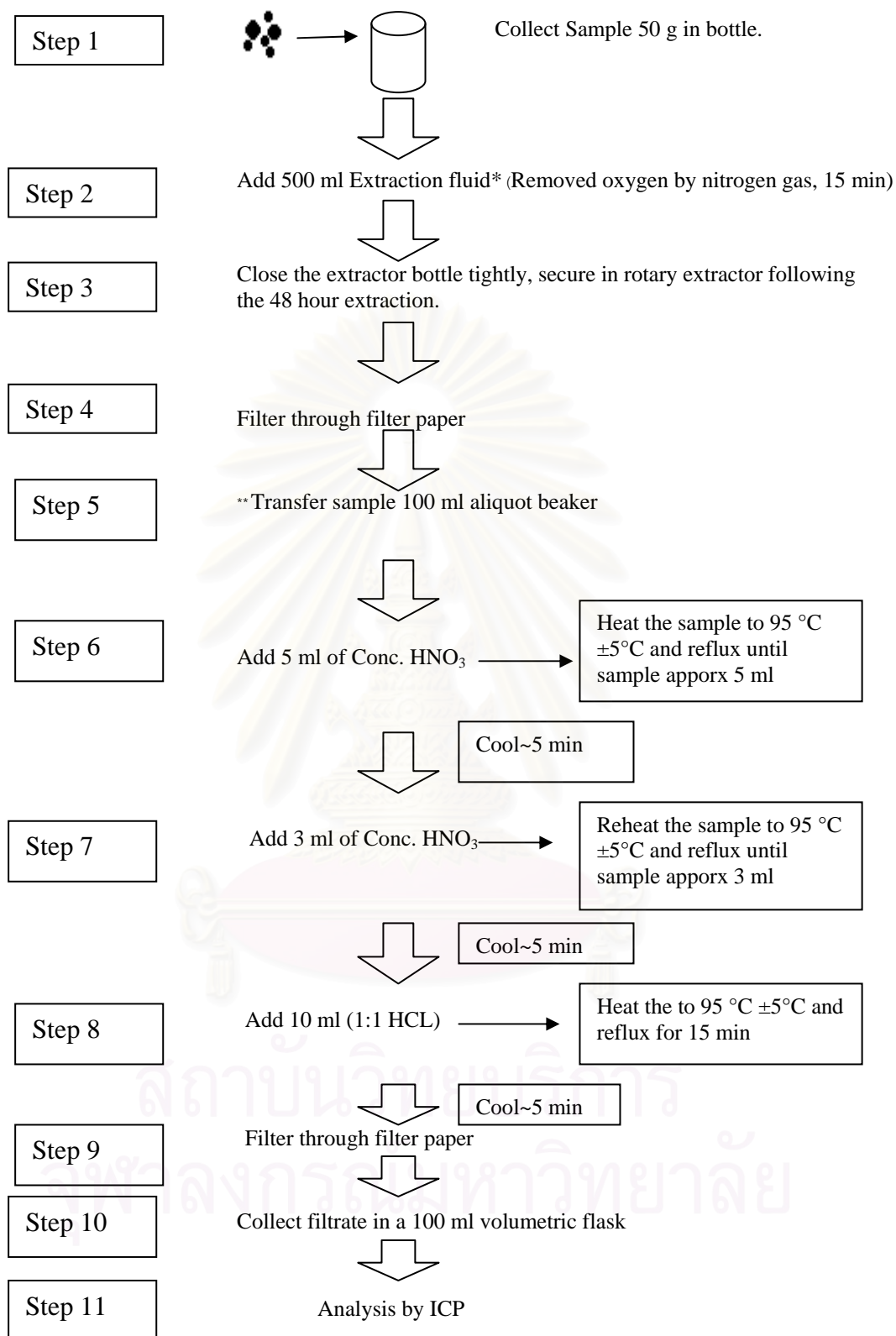
3.9 Analysis of Heavy Metal Leaching of heavy metal by Waste Extraction Test B.E. 2548 (WET)

This method was employed to analyze the hazardous material by extracted water. For this thesis, the clinker sample that different ratio of each heavy metal (Cr, Ni, and Zn) were analyzed to know the leaching of heavy metal out from the sample. The method was described by Figure 3.8.



Digest time: Step 2-7 approx. 345 min (5.75 hr.) per batch
 Total time: Step 1-10 approx. 375 min (6.25 hr.) per batch

Figure 3.7: Overall step of the EPA 3050 B method for analyzing total heavy metal



Remark : * Extraction fluid preparation : 0.2 M sodium citrate pH 5 ± 0.1 (Citric acid mix 4.0 N NaOH PH of fluid will be 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 3.8: Overall of Waste Extraction Test B.E. 2548

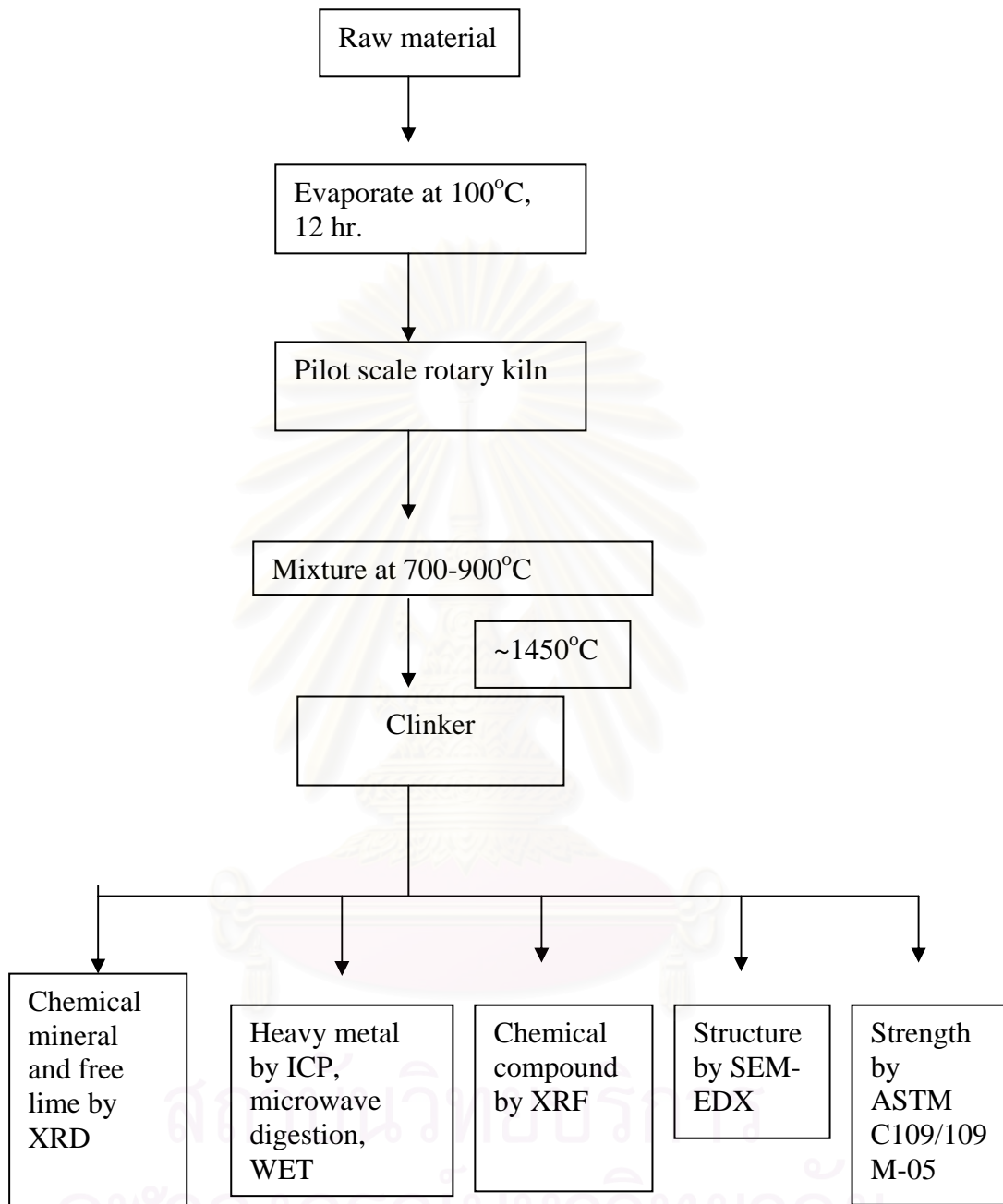


Figure 3.9: Overall steps to produce the clinker control

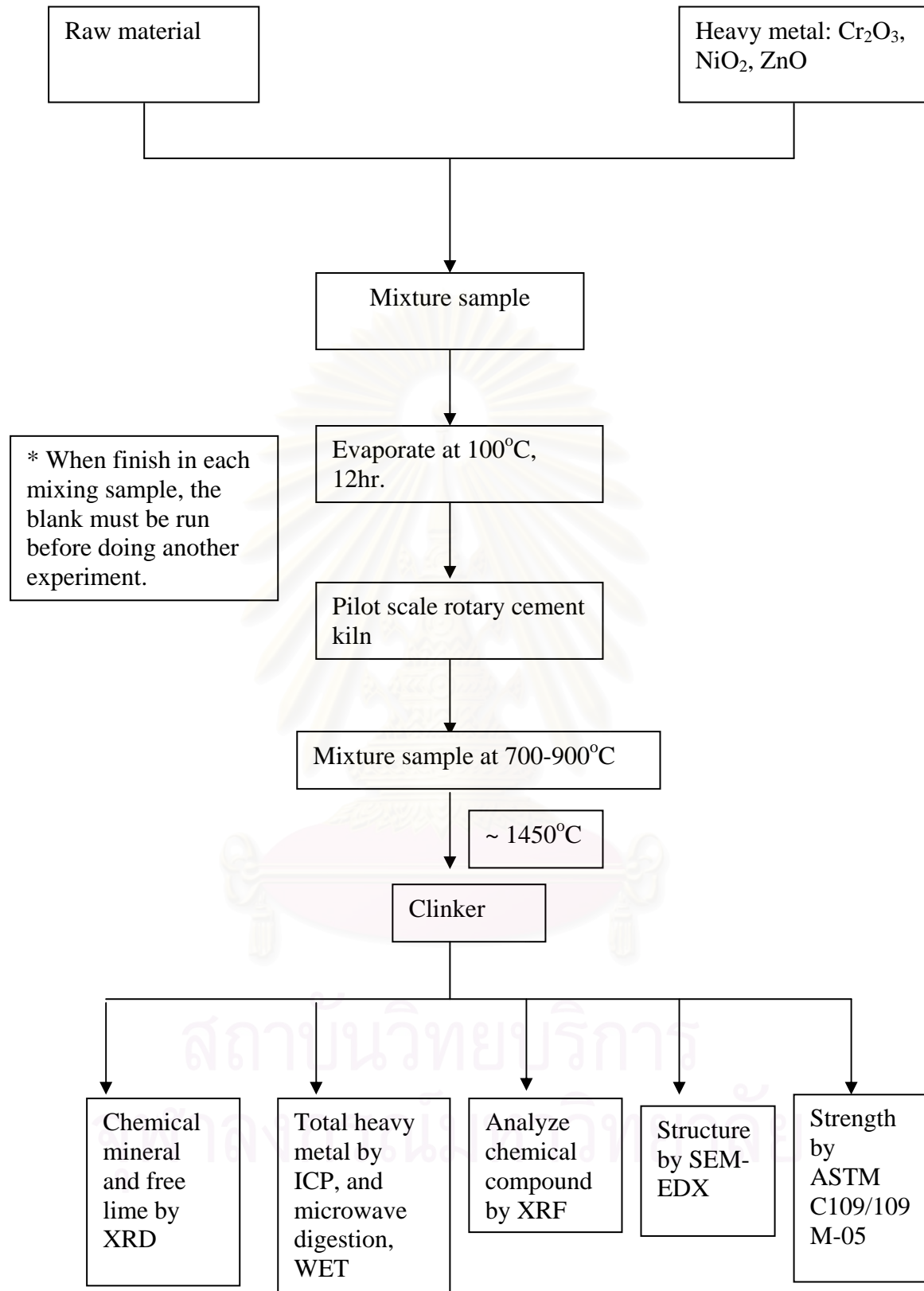


Figure 3.10: Overall steps to produce the mixture samples *

Chapter IV

Results and Discussion

The experimental results and the data analysis of the samples are presented in the following subsections.

4.1 Sample preparation

Kiln feed (raw meal) was collected from the Siam City Cement Public Company Limited (SCCC), from silo numbers 5 and 6 of factory number 3. X-ray fluorescence spectrometer (XRF) was used to analyze the chemical composition in the kiln feed to find their average values before being adjusted for lime saturation factor (LSF), silica modulus (SM), and alumina modulus (AM) that serve as indication of combinability and burn ability of feed mixtures in the pilot-scale rotary cement kiln. Table 4.1 shows the average chemical composition concentrations of LSF, SM, and AM in the kiln feed from silo numbers 5 and 6 of factory 3.

Table 4.1: Average chemical compositions percentages of the kiln feed from silo numbers 5 and 6 of factory number 3

Chemical composition	Kiln feed from silo 5, factory number 3	Kiln feed from silo 6, factory number 3
SiO ₂ (%)	13.33	12.64
Al ₂ O ₃ (%)	2.89	3.010
Fe ₂ O ₃ (%)	2.04	2.05
CaO (%)	44.04	44.61
MgO (%)	1.06	0.93
K ₂ O (%)	0.31	0.34
Na ₂ O (%)	0.07	0.03
SO ₃ (%)	0.18	0.20
P ₂ O ₅ (%)	0.06	0.06
TiO ₂ (%)	0.15	0.14
Mn ₂ O ₃ (%)	0.04	0.04
Cl (%)	0.01	0.01
LOI (%)	35.72	36.07
SUM (%)	99.88	99.98
LSF	104.76	110.81
SM	2.71	2.50
AM	1.40	1.47
Na _{eq} (%)	0.27	0.25
BF	125.65	131.84

Since samples taken from different time and different silos produced different chemical compositions, all of collected kiln feed samples were mixed in the mixing rotary machine to create uniform samples. Table 4.2 shows the average chemical

compositions of the mixed kiln feed. LSF was 105.41%, whereas 2.65% and 1.35% were the percent concentrations of SM and AM

Table 4.2: Average chemical composition concentrations in the mixed kiln feed

Chemical composition	Mixed kiln feed
SiO ₂ (%)	13.23
Al ₂ O ₃ (%)	2.86
Fe ₂ O ₃ (%)	2.12
CaO (%)	44.06
MgO (%)	0.96
K ₂ O (%)	0.33
Na ₂ O (%)	0.05
SO ₃ (%)	0.22
P ₂ O ₅ (%)	0.06
TiO ₂ (%)	0.14
Mn ₂ O ₃ (%)	0.04
Cl (%)	0.01
LOI (%)	35.62
SUM	99.71
LSF	105.41
SM	2.65
AM	1.35
Na _{eq} (%)	0.26
BF	126.24

Next, a 2.5% of mixture between shale core and clay was added into the kiln feed to adjust the chemical compositions, LSF, SM, and AM to make the kiln feed suitable for burning in the pilot-scale rotary cement kiln. The chemical compositions of shale core, clay, and mixture of shale core and clay (25g:20g) were provided in Table 4.3, whereas, the chemical composition of the adapted kiln feed is described in Table 4.4.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.3: Chemical compositions of shale core, clay, and the mixture of shale core and clay (25g:20g)

Chemical composition	Shale core	Clay	Mixture of shale core and clay (25:20)
SiO ₂ (%)	76.17	35.21	57.86
Al ₂ O ₃ (%)	11.20	29.22	18.38
Fe ₂ O ₃ (%)	5.49	13.10	7.51
CaO (%)	3.67	1.21	3.71
MgO (%)	0.70	0.35	0.58
K ₂ O (%)	1.78	0.001	1.11
Na ₂ O (%)	0.09	0.001	0.01
SO ₃ (%)	0.16	0.03	0.12
P ₂ O ₅ (%)	0.07	0.07	0.09
TiO ₂ (%)	0.50	1.42	0.78
Mn ₂ O ₃ (%)	0.06	0.09	0.06
Cl (%)	0.001	0.001	0.001
LOI (%)	3.65	1.33	3.55
SUM	103.54	82.02	93.75
LSF	1.60	0.86	1.97
SM	4.56	0.83	2.24
AM	2.04	2.23	2.45
Na _{eq} (%)	1.25	0.001	0.74
BF	41.12	8.13	20.22

Table 4.4: Chemical composition of the kiln feed after the addition of a 2.5% mixture of shale core and clay

Chemical composition	Mixed kiln feed
SiO ₂ (%)	14.35
Al ₂ O ₃ (%)	3.29
Fe ₂ O ₃ (%)	2.30
CaO (%)	43.10
MgO (%)	0.97
K ₂ O (%)	0.34
Na ₂ O (%)	0.05
SO ₃ (%)	0.23
P ₂ O ₅ (%)	0.06
TiO ₂ (%)	0.16
Mn ₂ O ₃ (%)	0.04
Cl (%)	0.01
LOI (%)	34.88
SUM	99.78
LSF	94.57
SM	2.57
AM	1.43
Na _{eq} (%)	0.27
BF	114.53

Since the raw meal contained some heavy metals, US EPA method 3052B was used to digest the raw meals and ICP was used to determine the initial concentration of each heavy metal in the raw meal. The concentrations of heavy metals in the raw meal control are shown in Figure 4.5. Moreover, the total heavy metal concentrations in the raw meal after the addition of different ratios of three metal oxides were analyzed to know the leaching heavy metal values in the mixed raw meals. The results are shown in the Figures 4.6 to 4.8.

Table 4.5: Concentrations of heavy metals in the raw meal control, determined by EPA SW-846 Method 3052B and ICP

Metals	Concentration of heavy metal in the raw meal control (ppm)
Ca	33,370
Al	4,602
Fe	10,170
Cr	23.6
Zn	326
Ni	10.7

Table 4.6: Analysis of the Cr concentrations in the mixtures before burning in the pilot-scale rotary cement kiln by EPA SW-846 Method 3052B and ICP.

Concentration of Cr (ppm)	Concentration of Cr in the raw meal (ppm)
5,000	4,957
10,000	8,936
25,000	22,190
50,000	35,670

Table 4.7: Analysis of Ni concentrations in the mixtures before burning in the pilot-scale rotary cement kiln by EPA SW-846 Method 3052B and ICP.

Concentration of Ni (ppm)	Concentration of Cr in the raw meal (ppm)
1,000	2,840
5,000	6,932
10,000	13,550
15,000	20,760

Table 4.8: Analysis of Zn concentrations in the mixtures before burning in the pilot-scale rotary cement kiln by EPA SW-846 Method 3052B and ICP.

Concentration of Zn (ppm)	Concentration of Cr in the raw meal (ppm)
3,000	2,724
10,000	6,195
25,000	19,220
50,000	34,900

Because the raw meal and heavy metal were both solid in form, they were difficultly mix to the same form and attached all molecule in raw meal. Therefore, these results were used for the burning process.

4.2 Moisture content and LOI analyses

The moisture content and LOI are good indicators to show percent loss of the weight of kiln feed and samples before burning at 1450°C. After burning, most of the weight loss could be attributed to evaporation of moisture. The weight of the resulting control kiln feed was reduced by 0.206%. The weight of the samples containing Cr₂O₃ was reduced by 0.098%, even at the higher concentrations of Cr₂O₃. Similarly, the kiln feed samples containing ZnO lost 0.155% of weight. However, the moisture content reduction in the weight of the samples containing NiO was higher at about 0.248%. The loss of calcinations products on ignition of the pure kiln feed was 4.790. Evaporation of carbon dioxide and the elements at a low boiling point caused of the loss of weight in the kiln feed and increased percent concentration of chemical oxide in the kiln feed. The weight of the ZnO and kiln feed sample mixtures reduced as the ZnO concentration increased. High temperatures may have affected the Zn inside the kiln feed. The weight of kiln feed with Cr₂O₃ did not change even when the metal oxide contents were increased or decreased in the feed. The reason was that the boiling point of Cr and Ni were high (2671°C for Cr and 2913°C for Ni). The weight of the kiln feed with NiO was gradually increased when a high concentration of Ni was added into the raw meal. The average loss on ignition of the mixture containing Cr₂O₃ was 5.183%. As for the mixture of NiO with kiln feed, the average loss on ignition percentage was 4.695%.

Table 4.9: Results of moisture content and loss on ignition percentages of kiln feed with different concentrations of Cr

Concentration of Cr (ppm)	Moisture content (%)	Loss on ignition (%)
5,000	0.11	5.00
10,000	0.09	5.32
25,000	0.10	5.05
50,000	0.09	5.36
Average	0.098	5.18

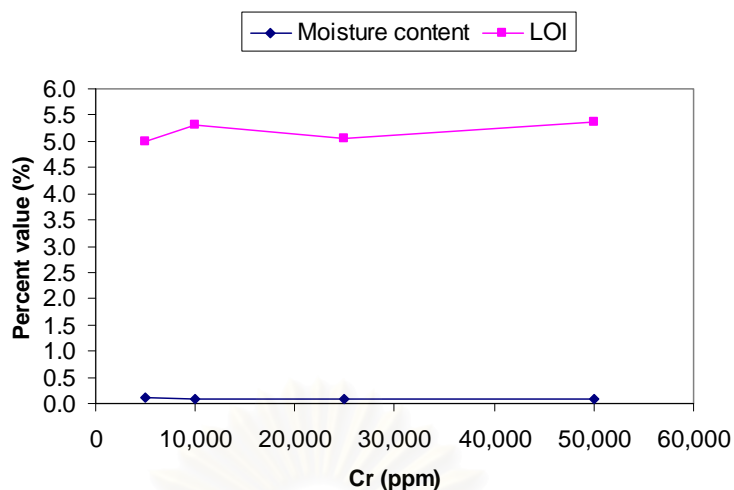


Figure 4.1: Moisture content and LOI of kiln feed with different concentration of Cr

Table 4.10: Results of the moisture content and loss on ignition percentages of kiln feed at different concentrations of Zn

Concentration of Zn (ppm)	Moisture content (%)	Loss on ignition (%)
3,000	0.19	4.30
10,000	0.15	4.99
25,000	0.16	5.55
50,000	0.12	20.79
Average	0.155	-

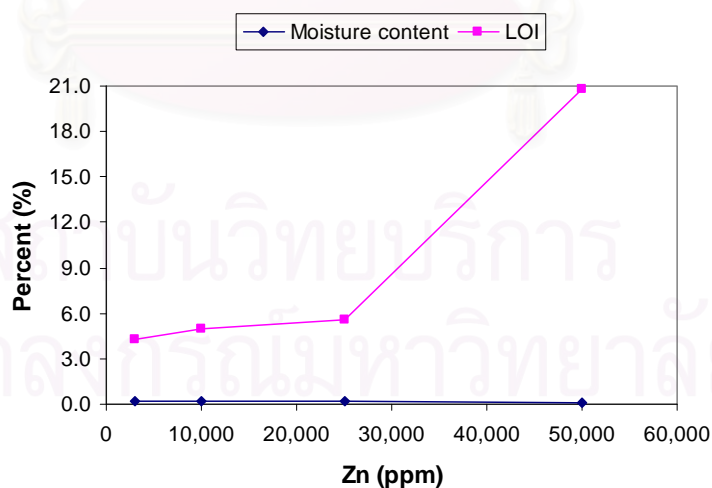


Figure 4.2: Moisture content and LOI of kiln feed with different concentrations of Zn

Table 4.11: Results of moisture content and loss on ignition percentages of kiln feed at different concentrations of Ni

Concentration of Ni (ppm)	Moisture content (%)	Loss on ignition (%)
1,000	0.18	4.34
5,000	0.23	4.52
10,000	0.28	4.80
15,000	0.30	5.12
Average	0.248	4.70

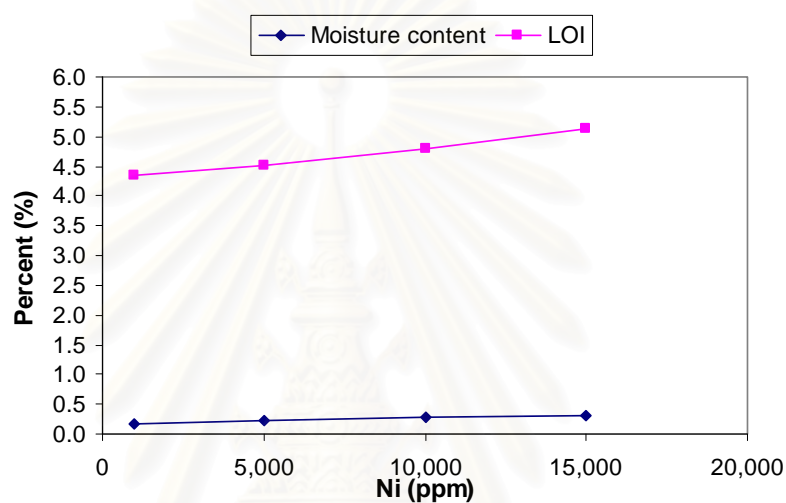


Figure 4.3: Moisture content and LOI of kiln feed with different concentrations of Ni

4.3 Burning in the pilot- scale rotary cement kiln

In this study, the temperature used in the burning process was important because it indicated whether the clinker set and formed completely. A thermocouple was used to measure the temperature inside the pilot-scale rotary cement kiln. Since the thermocouple was set in the feed product part of the pilot-scale rotary cement kiln, it was difficult to check the rotary kiln. Different parts of the pilot-scale rotary cement kiln were given different temperature. The static method was used to check the suitable zone for the burning process. The five crucibles containing kiln feed were set in the different locations of the rotary kiln as shown in Figure 4.4. The temperature inside was measured by the thermocouple, and the temperature was set at 1100°C for 60 minutes. Free lime, C_3S , C_2S , C_3A , and C_4AF were measured by XRF to check the setting form of the clinker. The result shown that at the location 3, close to the burner yielded the most suitable clinker compositions when compared to the other parts. The results of the static process are shown in Table 4.12.



Figure 4.4: The positioning of the five crucible glasses for the static burning process

Table 4.12: Analysis of chemical mineral in clinker produced by the static method

Location	Condition	Temperature (°C)	Mineral composition				
			C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)	Free lime (%)
1	Static	1,100	75.54	3.26	10.54	8.57	6.03
2	Static	1,100	70.03	5.56	11.87	8.95	3.92
3	Static	1,100	62.13	16.53	7.68	10.33	0.69
4	Static	1,100	65.20	13.72	7.49	10.22	0.73
5	Static	1,100	58.49	21.05	7.77	10.35	2.64

After the suitable part was found, the kiln feed control was burned under the dynamic condition. When the thermocouple, placed at the inlet part, indicated the temperature was 1,100 °C, the control kiln feed was added, and burned for around 40 minutes. The results of the clinker composition from burning process are shown in Table 4.13

Table 4.13: Composition of the control clinker after the dynamic process

Sample	Temperature (°C)	Mineral composition				
		C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)	Free lime (%)
Control	1,100	64.41	10.45	7.62	10.25	1.46
Quality guideline values (SCCC, 2008)	-	63-70	7-14	6.5-8.5	9-11	≤1.8



Figure 4.5: Clinker inside the pilot-scale rotary cement kiln



Figure 4.6: Thermocouple at the inlet part of the pilot-scale rotary cement kiln

4.4 The content of free lime

The free lime content is a good indicator of what happens during the burning process. A low concentration of free lime means an improvement in the ability of the burning process and the complete form in the clinker product. In the contrast, a high concentration of free lime indicates deterioration during the burning process, which can cause the clinker to not set completely, and cause the cement to break easily. The percent concentration of free lime was reduced when the Ni concentration the clinker increased to 1.0 % wt. The percent gradually increased in the clinker with Ni concentration of 1.5 % wt. 1.69 % was the percent free lime in the clinker with a 0.1% wt. Ni , whereas, 1.63%, 0.83%, and 1.01 % were the free lime in the clinker at the respective Ni ratios of 0.5%, 1.0%, and 1.5% wt. Free lime slightly decreased when the concentration of Zn in the clinker increased. At the 0.3%, 1.0%, 2.5%, and 5.0 %wt. of Zn, the free lime content in the clinker was 1.29%, 0.93%, 0.60%, and 0.53%, respectively. On the other hand, high concentrations of Cr were found to

increase the free lime of clinker. However, clinker with 5.0% of Cr reduced the free lime in the clinker product. 1.64%, 1.58%, 1.83%, and 1.17% were the free lime contents of the clinker samples with the Cr ratios of 0.5%, 1.0%, 2.5%, and 5.0 %wt. Some of the effects of heavy metal on clinker have been described by other authors. Taweekitwanit (2004) found the free lime increased to 4.01% in a mixture of kiln feed and 2.0 % wt of Cr, whereas, the increased concentration of Ni and Zn reduced the 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 in clinker. 2.0 wt% of Zn in the kiln feed sample gave 0.365% of the free lime content in clinker. Stephan et al (1999) found that high concentrations of Ni and Zn permanently reduced the concentration of free lime in clinker. However, at 2.5 wt% of Cr, the free lime content in the clinker increased to 3.2%. Malozhon et al (1971) found an extremely high rise in free lime content of a mixture of kiln feed and 1.5% of Cr. Older et al (1980), Bordoloi et al (1998), and Knofel et al (1978) have found that high concentrations of Zn in the kiln feed can reduced the free lime content and improve the burning ability of kiln feed.

Table 4.14: Free lime in the clinker control and clinker samples

Clinker with Metal addition (ppm)	Free CaO (%)
Zn: 3,000	1.29
Zn: 10,000	0.93
Zn: 25,000	0.60
Zn: 50,000	0.53
Cr : 5,000	1.64
Cr : 10,000	1.58
Cr : 25,000	1.83
Cr : 50,000	1.17
Ni : 1,000	1.69
Ni : 5,000	1.63
Ni : 10,000	0.83
Ni : 15,000	1.01
Control	1.46

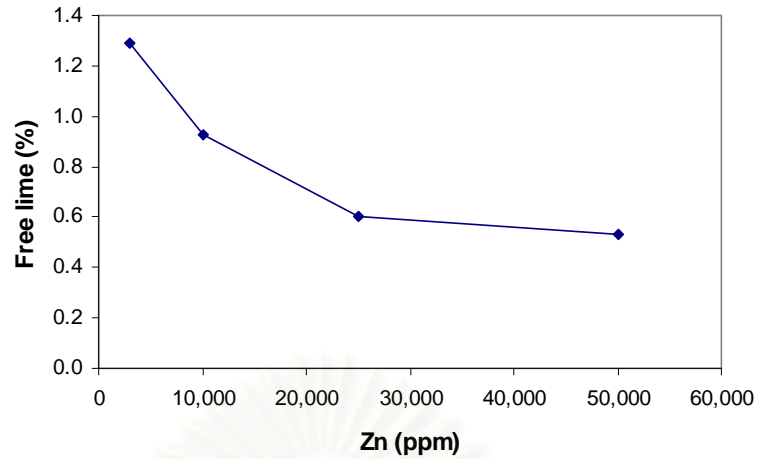


Figure 4.7: Free lime contents of clinker samples with different concentrations of Zn

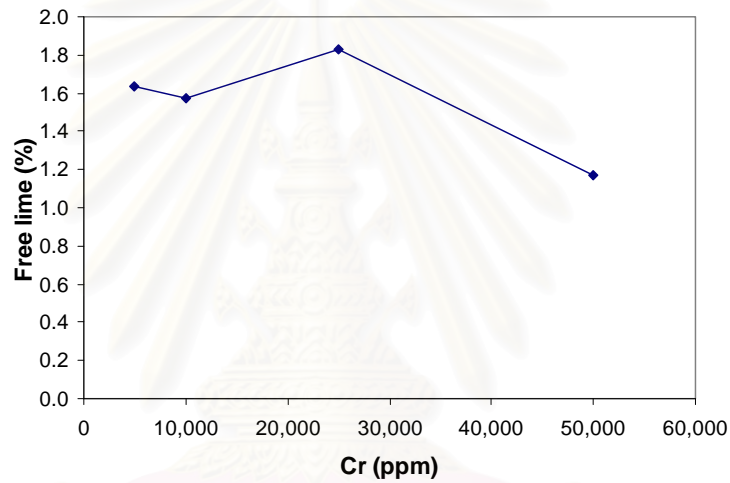


Figure 4.8: Free lime contents of clinker samples with different concentrations of Cr

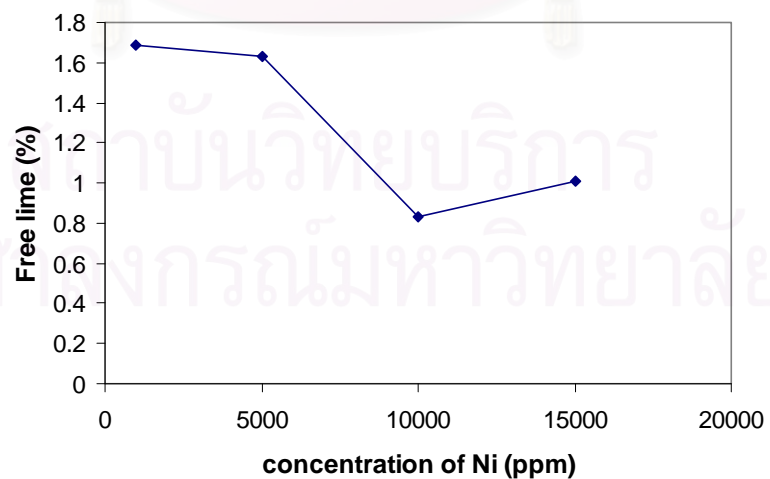


Figure 4.9: Free lime contents of clinker samples with different concentrations of Ni

4.5 The content of chemical oxide and chemical mineral

The XRF coupled with XRD spectrometer was used to analyze the concentrations of chemical oxides and mineral compositions of the pure kiln feed and the mixtures. Mineral compositions and chemical oxides indicate the degree of formation of clinker, whereas LSF, SM, and AM are related the burning process and cement compressive strength. Raw material recipes were optimized for suitable compositions and moduli in order to ensure complete formation of clinker in burning process. Chromium was found to affect alite phase because Chromium can prohibit the C_2S to change into C_3S . From the Table 4.15, it can be seen that increase in concentration of Cr in the raw meal caused C_3S reduction in the clinker phase. Furthermore, the color of clinker that containing Cr was green. As shown in Table 4.15, Ni did not have an effect on C_3S , C_3A , and C_4AF in the clinker phase even through it increased the concentration of NiO in the raw meal. However, Ni had little effect on the C_2S . The concentration of C_2S gradually decreased when the Ni concentration in the raw meal increased. The Zn concentration in the clinker was varied; a high concentration of Zn increased the concentration of C_4AF and reduced the concentration of C_3A . In the clinkers that contained 2.5% wt and 5.0% wt of Zn, the concentration of C_3S was still within the range but C_2S was high value too. Moreover, at 5.0% wt the color of the clinker was light brown. High concentration of Zn in caused of overburning in clinker product and set complete form at low temperature around 1,200°C (Hewlett, 1998). So, the clinker cannot stop reaction, it cause of C_2S remain high concentration inside product. Overburning also produced brown color in clinker (Hewlett, 1998).

Table 4.15: Mineral compositions in clinker samples by XRD

Clinker samples with different conc. of heavy metals (ppm)	Mineral compositions (%)			
	C_3S	C_2S	C_3A	C_4AF
Cr: 5,000	49.53	24.29	3.82	10.86
Cr: 10,000	40.61	27.20	4.38	11.03
Cr: 25,000	20.14	40.33	4.52	11.33
Cr: 50,000	14.95	34.61	4.71	13.23
Zn: 3,000	60.44	19.23	4.81	10.24
Zn: 10,000	61.49	33.49	4.87	11.24
Zn: 25,000	67.06	46.82	2.02	14.31
Zn: 50,000	64.03	54.24	1.57	16.26
Ni: 1,000	62.35	15.84	8.18	10.91
Ni: 5,000	62.23	14.96	7.98	10.94
Ni: 10,000	62.09	13.68	8.13	10.91
Ni: 15,000	61.29	13.43	7.96	10.97

There are a few research projects related to the effect of heavy metal on the mineral phases of clinker. Stephan et al (1999) found that 2.5% of Cr inhibited the C_2S reaction with CaO to set the C_3S , causing low C_3S of only 21.9%. However, 2.5% of Zn induced a small increase in C_3S and a corresponding decrease of C_2S . The Mineral contents in the clinker samples were in the acceptable ranges. Butt et al

(1969) found high Cr values increased the concentration of C_2S into clinker. Similar to the studied of Barros (2004), the addition of Cr into the kiln feed sample inhibited C_2S to further form C_3S , while Ni did not have an effect on the minerals in the clinker. Malozhon et al (1971) found that the concentration of C_3S was reduced when Cr was added up to around 1.5% wt. Older et al (1980) found increased concentrations of C_3S came from the substitution of Zn for Ca. The study from Andrade found that 1% of ZnO did not have an effect on the chemical minerals in the clinker. The values were quite similar when compared to the chemical minerals in the clinker that were produced from pure kiln feed. Furthermore, in an investigation by Knofel (1978) up to 4.0% wt of Zn did not affect the C_3S and C_2S , but increased concentration of C_4AF . However, it reduced concentration of C_3A in the clinker. Kakali (1995) found that 3% wt. of ZnO in raw meal can change the clinker color from black to brown color.

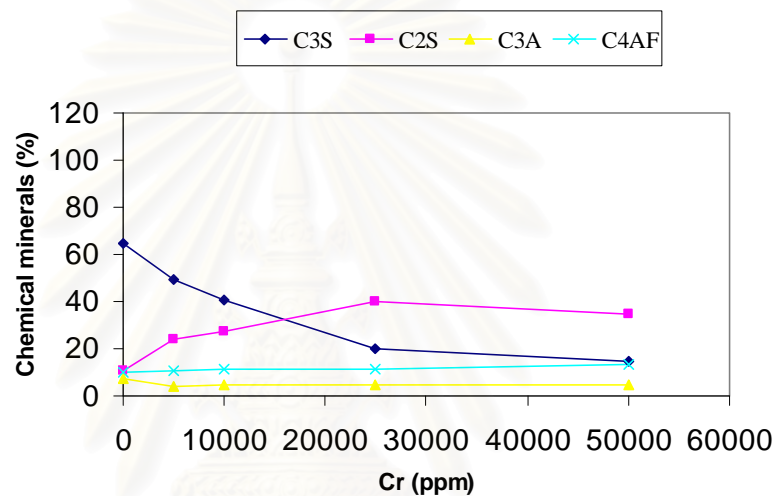


Figure 4.10: Minerals in clinker samples with different concentrations of Cr

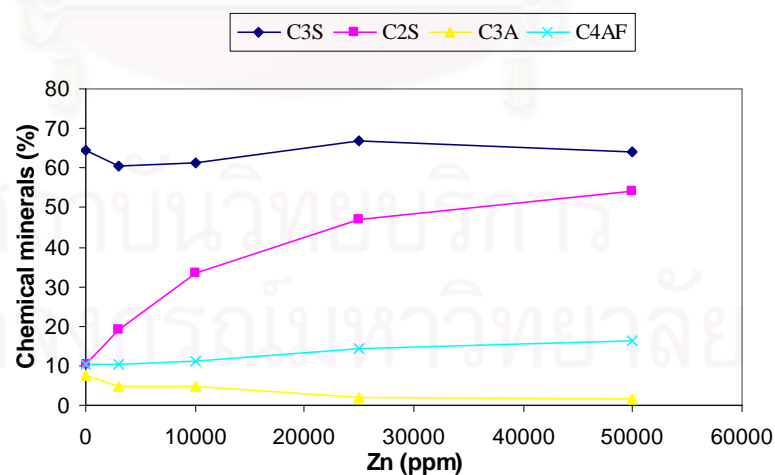


Figure 11: Minerals in clinker samples with different concentrations of Zn

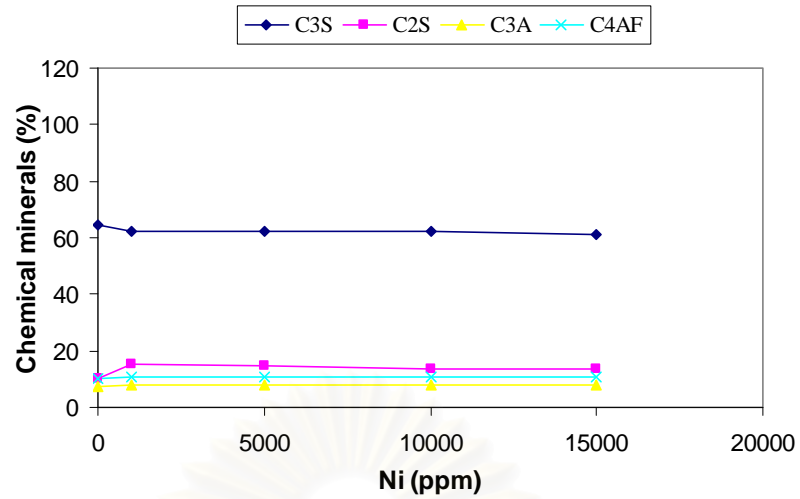


Figure 4.12: Minerals in clinker samples with different concentrations of Ni



Figure 4.13: Brown color of clinker that contains 5.0% wt of Zn

Chemical oxides, LSF, SM, and AM in the clinker samples were analyzed by the XRF instrument. The results are provided in Table 4.16.

Table 4.16: Concentrations of chemical oxides, LSF, SM, and AM of the clinker samples at different concentrations of each heavy metal and the control

Clinker samples (ppm)	Chemical oxides (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	LSF	SM	AM
Control	20.63	5.77	3.05	66.55	95.41	2.34	1.89
Cr: 5,000	21.56	4.77	3.19	65.29	95.93	2.71	1.50
Cr: 10,000	20.58	4.80	3.16	64.28	98.38	2.59	1.52
Cr: 25,000	19.10	4.51	2.85	62.51	103.08	2.60	1.58
Cr: 50,000	16.31	4.09	2.47	58.20	111.72	2.49	1.65
Zn: 3,000	22.30	4.99	3.37	65.58	93.01	2.67	1.48
Zn: 10,000	21.55	5.42	3.35	64.57	93.72	2.46	1.62
Zn: 25,000	20.34	4.61	3.37	63.32	98.05	2.55	1.37
Zn: 50,000	17.56	4.17	3.47	60.06	106.60	2.30	1.20
Ni: 1,000	21.93	5.38	3.59	66.43	94.78	2.44	1.50
Ni: 5,000	21.59	5.31	3.60	65.66	95.08	2.42	1.48
Ni: 10,000	21.11	5.36	3.59	64.81	95.64	2.36	1.49
Ni: 15,000	20.81	5.31	3.60	63.97	95.65	2.33	1.47
Standard	18-22	4-6	2-4	55-65	95+1	≥2.2	≥1.5

4.6 Analysis of total heavy metals by EPA 3052B

EPA 3052 was the method used for analyzing the concentrations of heavy metal inside the clinker product. Tables 4.18 to 4.20 show the concentrations of heavy metals inside the clinker products. Due to the evaporation of easily volatilized compounds in the raw meal during the burning process, the concentration of heavy metal in the clinker was higher than the heavy metals inside the kiln feed before the burning process.

Table 4.17: Analysis of the concentrations of heavy metals in the control clinker after burning in the pilot- scale rotary cement kiln by EPA 3052B.

Heavy metal	Heavy metal concentration of heavy metal in the control clinker (ppm)
Ca	44,730
Al	22,900
Fe	14,830
Cr	65
Ni	21.2
Zn	297

Table 4.18: Analysis of the concentrations of Cr in the clinker after burning in the pilot- scale rotary cement kiln by EPA 3052B.

Ratios of Cr (ppm)	Concentration of Cr in the clinker (ppm)
5,000	8,938
10,000	13,310
25,000	24,230
50,000	39,820

Table 4.19: Analysis of the concentrations of Ni in the clinker after burning in the pilot- scale rotary cement kiln by EPA 3052B.

Concentration of Ni (ppm)	Concentration of Cr in the clinker (ppm)
1,000	1,940
5,000	10,330
10,000	13,420
15,000	27,150

Table 4.20: Analysis of the concentrations of Cr in the clinker after burning in the pilot- scale rotary cement kiln by EPA 3052B.

Concentration of Zn (ppm)	Concentration of Cr in the clinker (ppm)
3,000	2,674
10,000	7,758
25,000	24,550
50,000	49,320

Many studies found different concentrations of the heavy metals in the clinker. The high solubility condition of chemical compounds caused the easy leaching in the test. Cr can leach easily from a reaction between Cr and K in the raw meal to produce a new solution (K_2CrO_4). This solution had a +6 valence state, which caused it to be easily soluble (Taweekitwanit, 2004).

4.7 The XRD and SEM analyses of phases of heavy metals in the clinker

These methods were used to determine the major components in the clinker samples and the characteristics of the three heavy metals in the clinker phase. A high concentration of each three heavy metal was chosen for analysis. By SEM analysis, the spectrum from the instrument was shot into random positions on the samples. In the clinker sample that contained 50,000 ppm of Cr, it had an effect on C_3S and C_2S . The chromium was usually trapped by C_3S , and C_2S as followed to the Figure 4.14. Spectrum number 1 is the position of belite, whereas spectrum number 3 is alite. The concentration of Cr was also trapped by C_3A and C_4AF . By XRD analysis, it was determined that Cr reacted with calcium and aluminum to produce Calcium aluminum chromium oxide ($Ca_6Al_4Cr_2O_{15}$). Previously, Murat and Sorrentino (1996) reported that Cr reacted with Al and Fe in the clinker phase, and produces a new solution containing calcium aluminate, calcium chloroaluminate, gehlenite calcium chromate and two types of ferrites. Opoczky and Gavel (2004) found that Cr was contained in C_3S and C_2S and made their size of them larger than usual (> 100 and $80-90\mu m$, respectively). The incorporation of Cr in C_3S and C_2S also produced the green color in clinker. Stephan et.al (1999) found that Cr reacted with K and produced K_2CrO_4 and $K_2Cr_2O_7$.

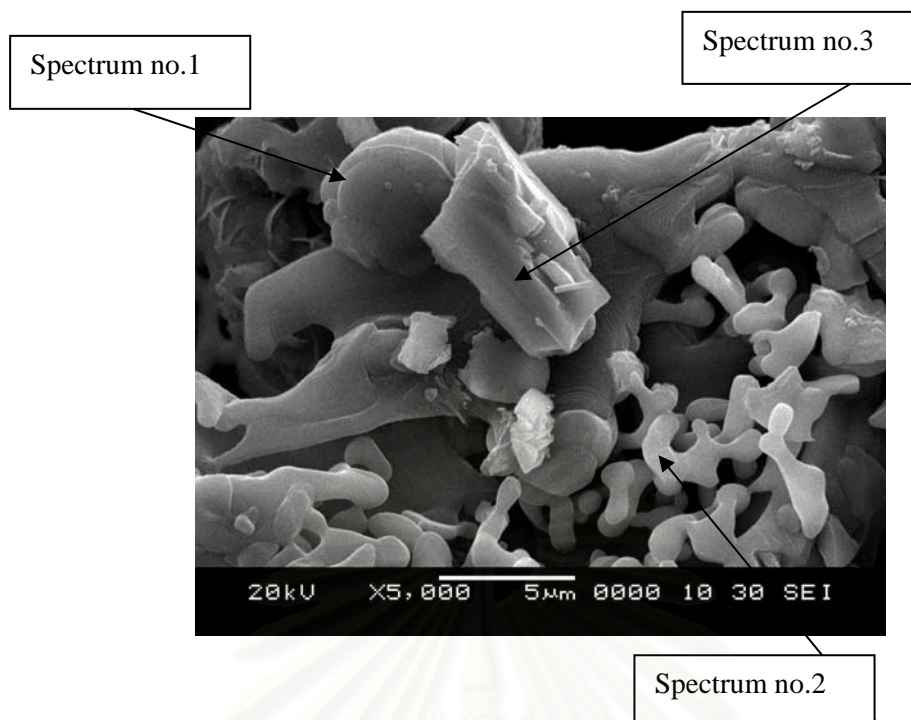


Figure 4.14: Analysis of Cr in the clinker phase by SEM-EDS

Table 4.21: Concentrations of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.1

Element	Weight (%)
C	2.89
O	49.66
Si	6.09
Ca	28.55
Cr	12.81
Total	100

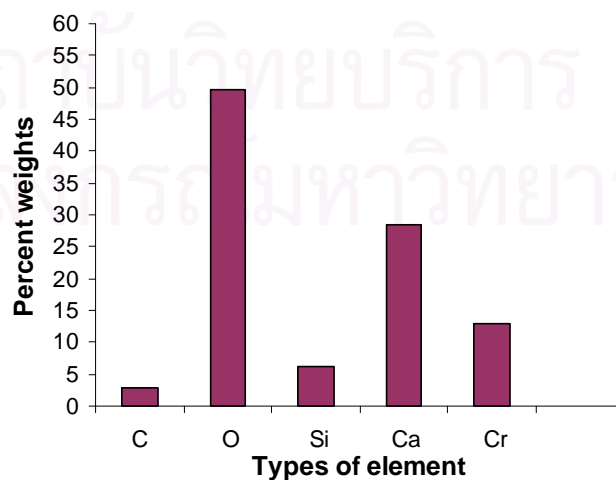


Figure 4.15: Percent weights of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.1

Table 4.22: Concentrations of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.2

Element	Weight (%)
C	4.52
Ca	22.34
Cr	10.27
Mg	3.89
Al	7.26
Fe	6.61
O	45.39
Total	100

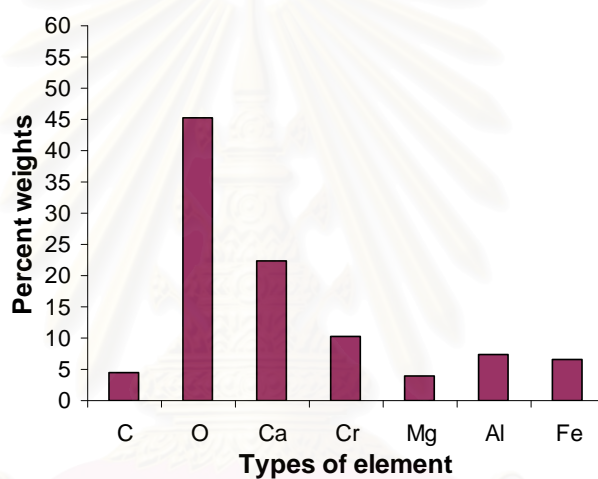


Figure 4.16: Percent weights of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.2

Table 4.23: Concentrations of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.3

Element	Weight (%)
C	3.97
Ca	15.97
Cr	32.17
Mg	7.66
Al	1.07
Fe	0.76
O	37.65
Si	0.74
Total	100

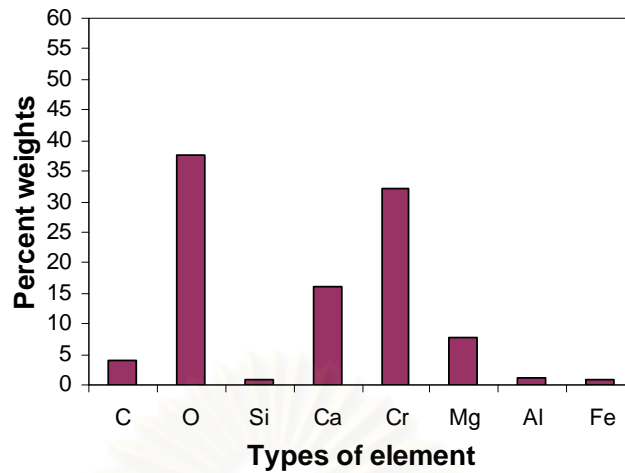


Figure 4.17: Percent weights of elements in the clinker phase (Cr: 50,000 ppm), Spectrum no.3

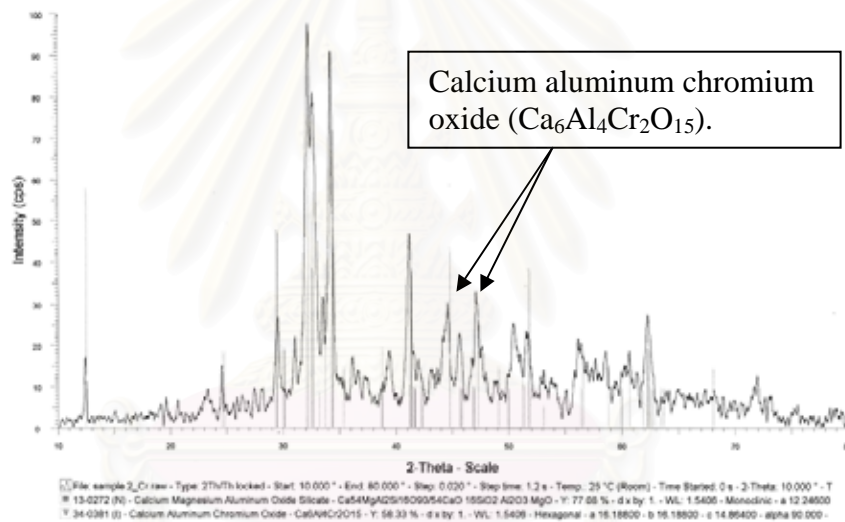


Figure 4.18: Analysis of Cr in the clinker phase by XRD

In the clinker sample containing 15,000 ppm of Ni, Ni was found in both C_3S and C_2S , and all of the chemical minerals were scarcely affected by Ni. By XRD analysis, Ni reacted with magnesium in the raw meal and produced magnesium nickel oxide solution ($\text{MgO} \cdot 4\text{NiO} \cdot 6\text{O}$). The results show that Mg influenced Ni in the clinker phase. Opoczky and Gavel (2004) found that Ni incorporated into C_3S and C_2S and took the place of the Ca^{2+} ion. Since the size of the Ni^{2+} ion is smaller than that of the Ca^{2+} ion, it does not cause the deformation of the C_3S and C_2S lattice. Stephan et.al (1999) found the Ni was reacted with Mg in the burning process and produced an MgNiO_2 solution in the clinker phase.

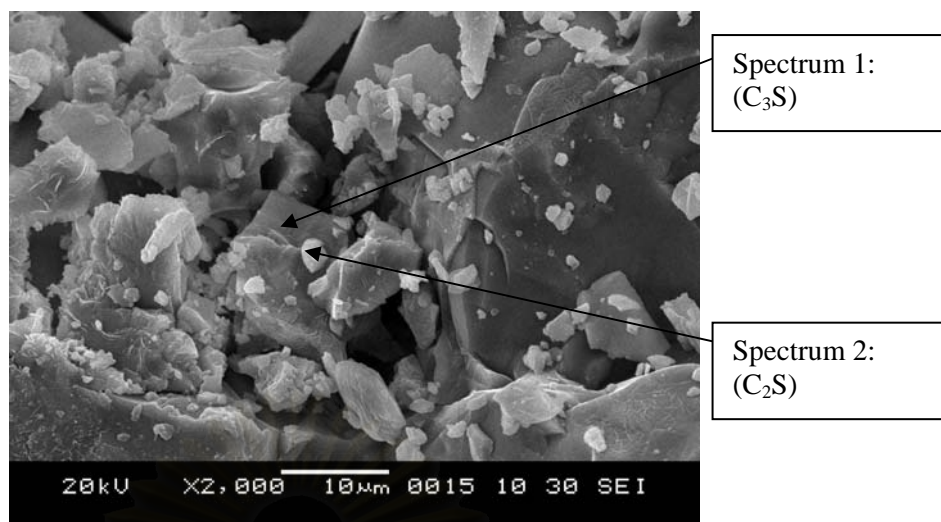


Figure 4.19: Analysis of Ni in the clinker phase by SEM-EDS

Table 4.24: Concentrations of elements in the clinker phase (Ni: 15,000 ppm), Spectrum no.1

Element	Weight (%)
C	4.15
Ca	31.66
Ni	1.89
Fe	9.79
Al	8.37
Si	4.74
O	39.41
Total	100

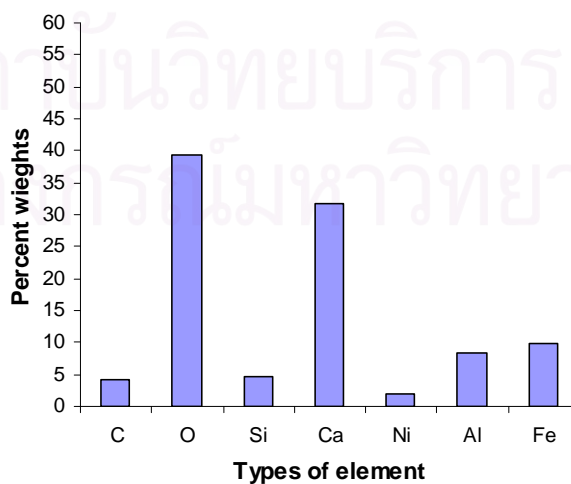


Figure 4.20: Percent weights of elements in the clinker phase (Ni: 15,000 ppm), Spectrum no.1

Table 4.25: Concentrations of elements in the clinker phase (Ni: 15,000 ppm), Spectrum no.2

Element	Weight (%)
C	2.80
Ca	34.30
Ni	2.19
Ti	0.50
Al	7.64
Fe	10.60
O	38.26
Si	3.72
Total	100

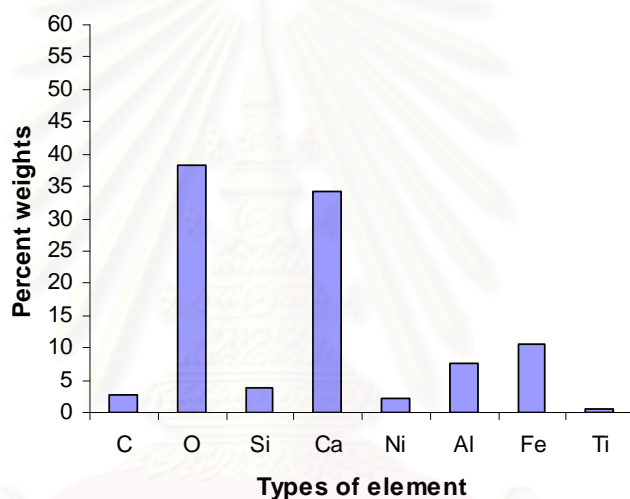


Figure 4.21: Percent weights of elements in the clinker phase (Ni: 15,000 ppm), Spectrum no.2

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

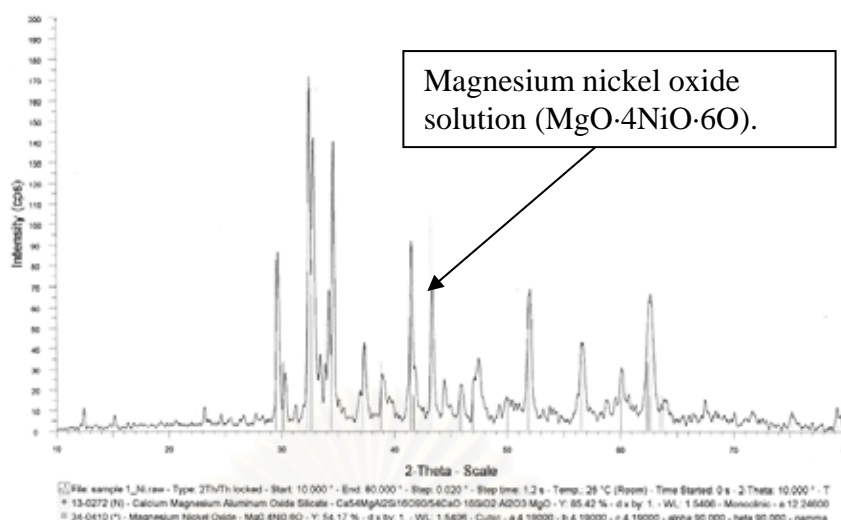


Figure 4.22: Analysis of Ni in the clinker phase by XRD

At the 50,000 ppm of Zn, the clinker structure was found to be affected. It created large-size C_3S . However, it was difficult to indicate the other chemical mineral that went into the clinker phase. 5.12%, 2.51%, and 2.88% were the respective percent weights of spectrum no.1, spectrum no.2, and spectrum no.3. The percent weights of the other elements in each three spectrum were described in Tables 4.26 to 4.28. XRD analysis showed that Zn reacted with iron, manganese, and chromium in the sample to get zinc iron manganese chromium oxide ($Zn [Fe_{0.5}Mn_{0.5}Cr] O_4$). When Zn reacted with Mn can accelerate the overburning reaction (Hewlett, 1998). Moreover, MAD-10 Feldspar was found in the clinker. It produced a brown color into the clinker because the structure of MAD-10 Feldspar is dark red crystal (Möller, 2008). Previously, Murat and Sorrentino (1996) found that Zn reacted with Fe in clinker and created large size of C_3S . Stephan et al (1999) found that the clinker with 2.5 wt% of Zn produced a small increase of C_3S and a corresponding decrease of C_2S . Older et al. (1980) results agree with those of Stephan et al (1999); they both found that an increased in C_3S was due to the substitution of Zn for Ca. Andrade et al (2002) found that Zn was more easily incorporated into C_3S . The concentration of Zn in C_3S also produced a higher value than that of C_2S .

จุฬาลงกรณ์มหาวิทยาลัย

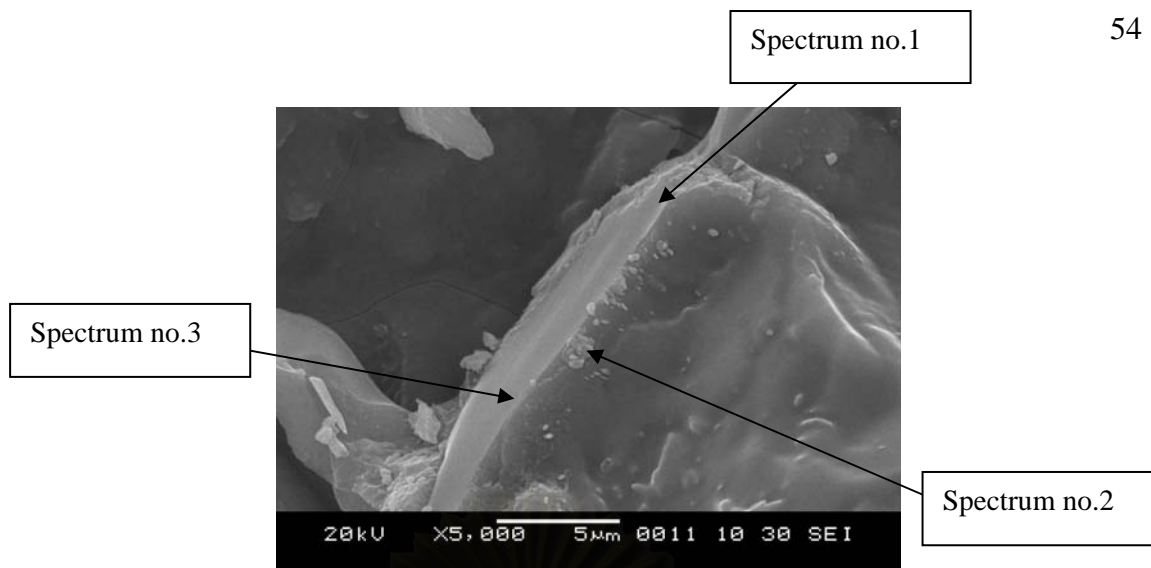


Figure 4.23: Analysis of Zn in the clinker phase by SEM-EDS

Table 4.26: Concentrations of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.1

Element	Weight (%)
C	7.40
Ca	30.83
Zn	5.12
Mg	0.58
Al	1.27
Fe	0.74
O	43.93
Si	8.83
K	1.27
Total	100

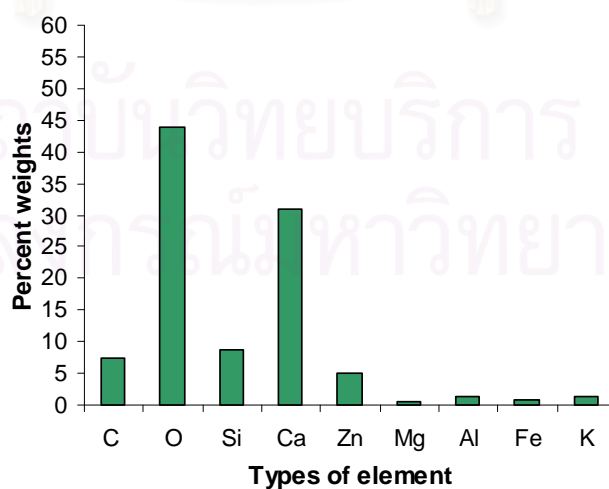


Figure 4.24: Percent weights of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.1

Table 4.27: Concentrations of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.2

Element	Weight (%)
C	6.30
Ca	34.53
Zn	2.51
K	1.03
Al	0.49
Si	9.04
O	46.09
Total	100

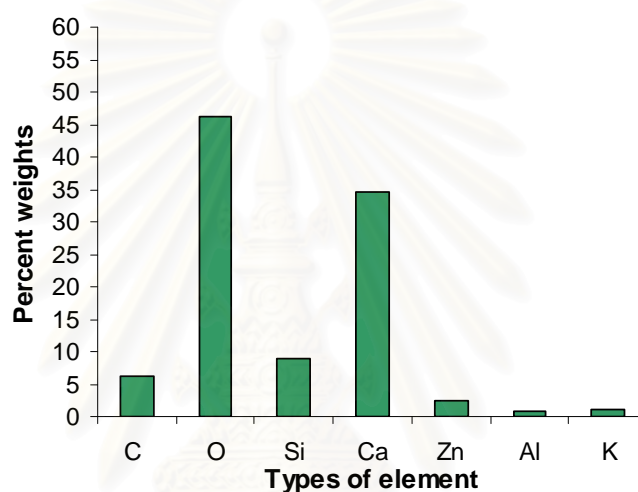


Figure 4.25: Percent weights of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.2

Table 4.28: Concentrations of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.3

Element	Weight (%)
C	5.77
Ca	29.06
Zn	2.88
Mg	0.44
Al	0.77
Fe	0.59
O	51.16
Si	8.33
K	1.00
Total	100

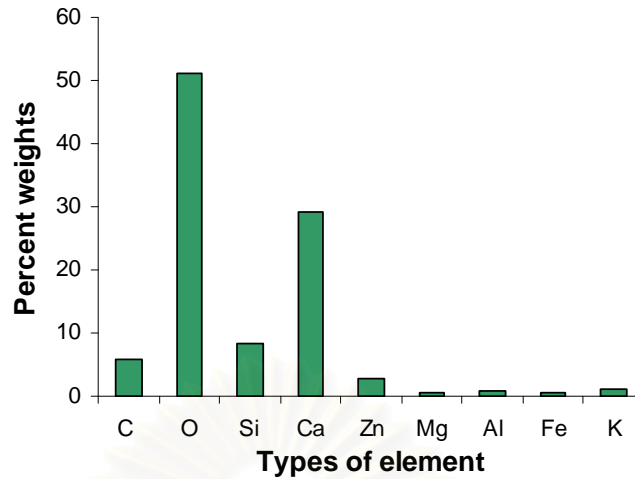


Figure 4.26: Percent weights of elements in the clinker phase (Zn: 50,000 ppm), Spectrum no.3

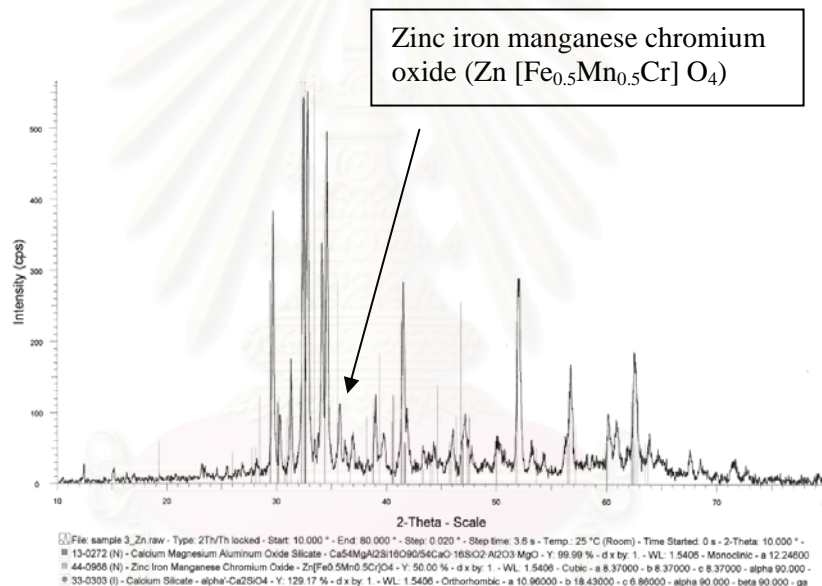


Figure 4.27: Analysis of Zn in the clinker phase by XRD

4.8 Waste Extraction Test (WET B.E. 2548)

The leaching test in the Notification of Ministry of Industry B.E. 2548 described a procedure involving putting 10 g of clinker sample through a leaching test and compare the resulting leachate concentration to the Soluble Threshold Limit Concentration (STLC) to determine if the clinker samples could be classified as hazardous wastes. At the leaching behavior in the control clinker, Cr, Ni, and Zn were not detected by this method. At the 0.5% wt. and 1.0 % wt. of Cr, the leaching behavior were increased, but the value of leaching behavior were reduced at 2.5% and 5.0% wt of Cr. 1.183, 2.452, 2.396, and 1.529 ppm were the respective leaching results of 0.5%, 1.0%, 2.5%, and 5.0 % wt. of Cr in the clinker sample. These leaching test results, however, were still within the range of the STLC (5 ppm). At the different ratios of Zn in the clinker, the leaching behavior of zinc in the sample was increased when the concentration of zinc in the clinker samples increased. At 0.3%,

1.0%, 2.5%, and 5.0% wt. of Zn, the respective leaching behavior results of leaching behavior were 0.262, 0.301, 0.442, and 0.589 ppm. The amounts of zinc in the samples still remain within the range of the STLC (250 ppm). The leaching behavior results for nickel on the samples were not detected by this method even through there was an increased concentration of nickel in the raw meal. Nickel was unlikely to be leached from the cement because the new nickel compound, identified as $MgNiO_2$ was a hydrated form that could not have reacted with water (Taweekitwanit, 2004).

Table 4.29: Analysis by the WET of leaching behavior on the heavy metals in the clinker control after burning in the pilot-scale rotary cement kiln.

Heavy metal in clinker control	Concentration of heavy metal in the clinker control (ppm)
Cr	ND
Ni	ND
Zn	ND

Table 4.30: Analysis by the WET of leaching behavior on the Cr in the clinker samples after burning in the pilot-scale rotary cement kiln.

Ratio of Cr (ppm)	Cr Leachant (ppm)	STLC, DIW (ppm)
5,000	1.18	5
10,000	2.45	5
25,000	2.40	5
50,000	1.53	5

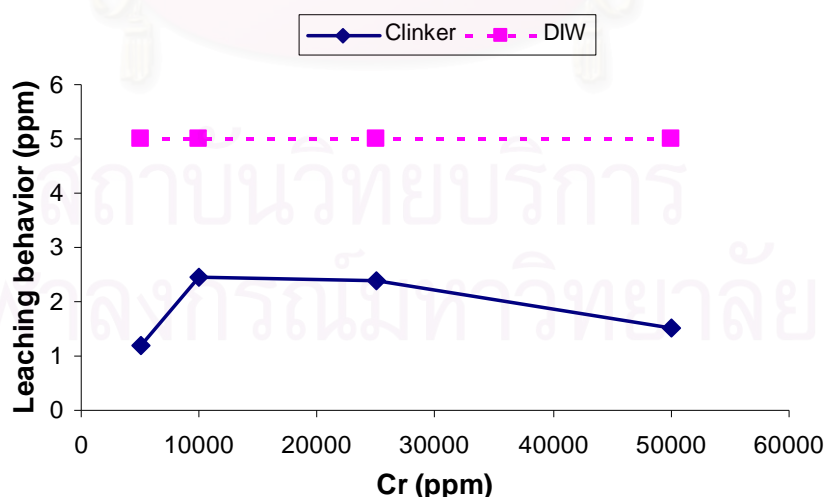


Figure 4.28: The leaching behavior of Cr in samples

Table 4.31: Analysis by WET of leaching behavior on the Zn in the clinker samples after burning in the pilot- scale rotary cement kiln.

The concentration of Zn (ppm)	Zn Leachant (ppm)	STLC, DIW (ppm)
3,000	0.26	250
10,000	0.30	250
25,000	0.44	250
50,000	0.59	250

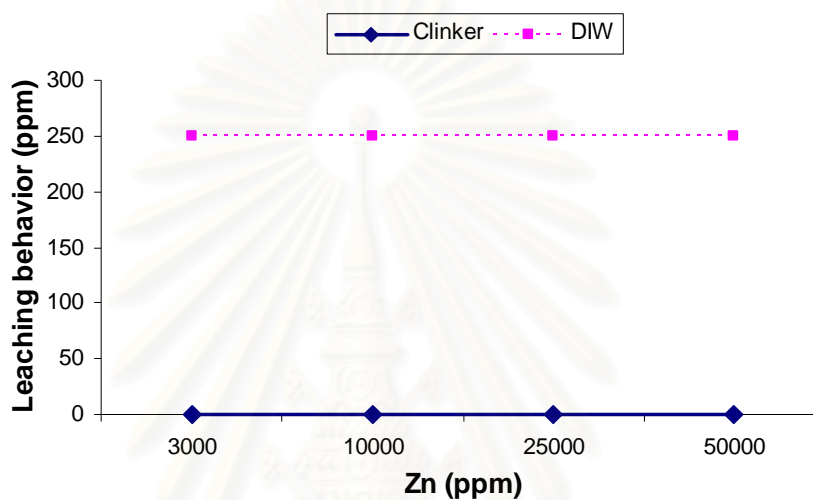


Figure 4.29: The leaching behavior of Zn in samples

Table 4.32: Analysis by WET of leaching behavior on the Ni in the clinker samples after burning in the pilot- scale rotary cement kiln.

The concentration of Ni (ppm)	Ni Leachant (ppm)	STLC, DIW (ppm)
1,000	ND	20
5,000	ND	20
10,000	ND	20
15,000	ND	20

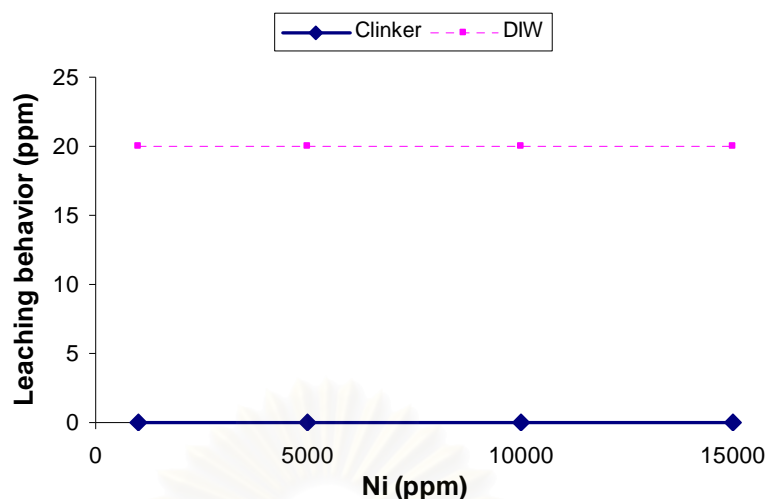


Figure 4.30: The leaching behavior of Ni in samples

From the previous study by Suvimol et al (2004), it was found that the leachate by the TCLP contained lower Cr than the limit specified by the US EPA. Low concentration of Zn was found in the leaching solution (0.5 mg/L) in work done by Murat (1996). He also found that pH indicated the leaching behavior of heavy metals in clinker. Taweekitwanit (2004) who performed the TCLP and the NFMI methods found that clinker containing 2.0 wt. % of Ni and Zn did not exceed the standard values. The leaching of Cr in chrome waste studied by Trezza and Scaini (2000) showed that Cr concentration around 1.17% at overall existing chrome. They also found the leaching of Cr to be lower than Argentine regulations (5 mg Cr/l) in spite of high Cr in samples. From the study of Espinosa and Tenorio (2000) that used the mixture between sludge and raw meal for the sample, they found leaching of Cr increased until 1.0 wt%. Then, Cr was undetectable at 3% wt. The reason was high concentration of Cr was trapped and immobilized in the clinker. The study from React et al. in 2003 found the leaching concentration of Ni of 0.02 ppm in synthetic clinker far below to Brazilian legal limit (0.25 ppm). The leaching solution of their test was 0.5N acetic acid with pH 5.0 ± 0.2 .

4.9 Compressive strength

Compressive strength is an important indicator used to determine the how cement mortar would withstand pressure. The strength of these clinker samples were compared against the Thai standard TIS no.12/ B.E.2528. Blaine value was one indicator that relates to compressive strength. To pass the Thai quality standard, the Blaine should be approximately $\geq 2,800 \text{ cm}^2/\text{g}$. The weight of each samples was around 800 g. Normally, the compressive strength increases over time. The results showed that a high chromium concentration in the clinker reduced the compressive strength of cement mortar. On the day 1 of curing, the compressive strengths of the cement mortar that containing 0.5%, 1.0%, 2.5%, and 5.0 % wt. of Cr were 131.02, 52.81, 29.86, and 3.09 kg/cm^2 . Whereas, 246.75, 150.04, 110.22, and 25.42 kg/cm^2 respectively were the compressive strength values at day 7 for the cement mortar that contained 0.5%, 1.0%, 2.5%, and 5.0% wt of Cr. In addition, at 28 days of curing, the compressive strength of cement mortar that contained 0.5, 1.0, 2.5, and 5.0 wt.% of Cr were 342.08, 222.09, 185.03, 90.31 kg/cm^2 respectively. The effect of Cr in the

cement mortar was described in previous studies. Murat and Sorrentino (1996) found that both 1.2 and 3.25 wt. % of Cr deteriorated compressive strength by the day 28. Stephan et al (1999) also found that the compressive strength was reduced at the 2.5 wt % of Cr in cement mortar.

Table 4.33: Compressive strength of mortars with different concentrations of Cr

Concentration of Cr (ppm)	Blaine (cm ² /g)	1-day strength (kg/cm ²)	7-day strength (kg/cm ²)	28-day strength (kg/cm ²)	Thai standard (minimum value, 7-day)	Thai standard (minimum value, 28-day)
Control	3,411	112.98	250.19	347.04	150	245
5,000	3,582	131.02	246.75	342.08	150	245
10,000	3,537	52.81	150.04	222.09	150	245
25,000	3,604	29.86	110.22	185.03	150	245
50,000	3,169	3.09	25.42	90.31	150	245

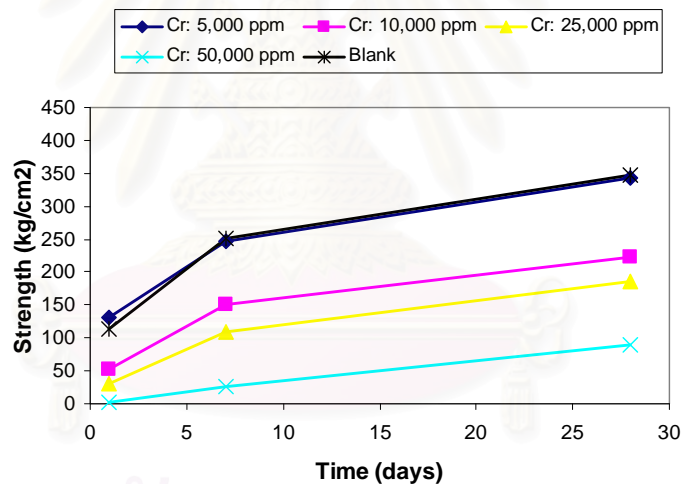


Figure 4.31: Compressive strengths of cement mortars with different Cr concentrations

The compressive strengths of cement mortars that contained different concentrations of Ni were found to increase. By day 28, the cement mortar containing 1% wt. of Ni had the highest compressive strength value when compared with cement mortar containing other concentrations of Ni. The compressive strengths of cement mortar that contained 1.5% wt of Ni was still high when compared to the samples with 0.1% and 0.5% wt. 71.55, 53.31, 118.90, and 83.33 kg/cm² were the compressive strength values at 1 day of curing for 0.1%, 0.5%, 1.0%, and 1.5 wt % of Ni in the cement mortars. the 7-day compressive strengths of the cement mortars that contained 0.1, 0.5, 1.0, and 1.5 wt% were 189.44, 184.34, 293.31, and 252.40 kg/cm², respectively. On the last day of curing (28th day), the performance was measured at 284.78, 291.53, 412.90, and 309.43 kg/cm², respectively. On the compressive

strength, cement mortar contained 1% wt of Ni gave the three different times test value higher than control. Previous studied have discovered that a high concentration of Ni can increase the compressive strength in cement mortar. Stephan et al (1999) found that the compressive strength of cement mortar contained 2.5 wt % of Ni was higher than the control after 28 days. They also found that $MgNiO_2$ produced from the reaction in burning process can improve the strength because it reduces the concentration of free Mg in the alite.

Table 4.34: Compressive strength of cement mortar with different concentration of Ni

Concentration of Ni (ppm)	Blaine (cm^2/g)	1 day (kg/cm^2)	7 days (kg/cm^2)	28 days (kg/cm^2)	Thai standard minimum value (7 days)	Thai standard minimum value (28 days)
Control	3,411	112.98	250.19	347.04	150	245
1,000	3,131	71.55	189.44	284.78	150	245
5,000	3,175	53.31	184.34	291.53	150	245
10,000	3,613	118.90	293.31	412.90	150	245
15,000	3,370	83.33	252.40	309.43	150	245

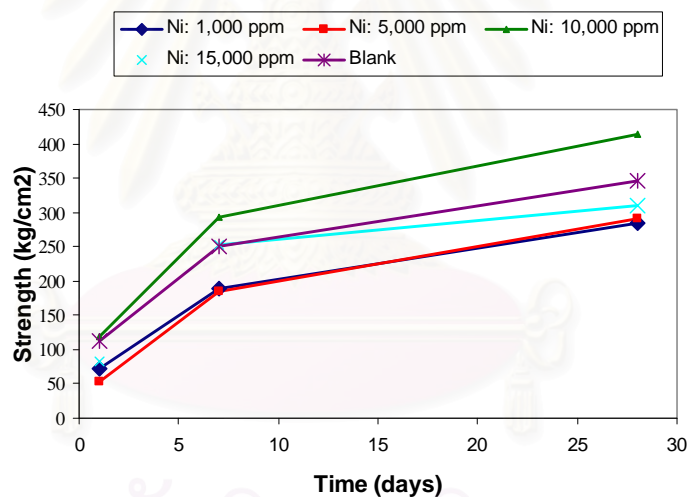


Figure 4.32: Compressive strengths of cement mortars with different Ni concentrations

At the curing ages of 1 and 7, the strength performance was found reduced when there were increased concentrations of Zn in the raw meal. However, the compressive strengths of cement mortars at day 28 that contained 1.0% and 2.5 wt % of Zn were higher than those of the cement mortars that contained 0.3% and 5.0 % wt of Zn. In addition, the compressive strength results of 0.3%, 1.0%, and 2.5 wt% of Ni at days 7 and 28 were higher than that of the control. This may be due to the effect of Zn in clinker that caused delayed setting, which may improve strength performance (Hewlett, 1998; and Stephan, 1999) of At day 1, the compressive strength of the cement mortar contained 0.3%, 1.0%, 2.5%, and 5.0 % wt of Zn were 129.65, 84.75, 17.67, and 15.01 kg/cm^2 , respectively. 308.47, 280.51, 263.97, and 255.01 were the compressive strength values of the cement mortar containing 0.3%, 1.0%, 2.5%, and

5.0% wt of Zn at day 7 . The performance at day 28 was 396.65, 403.95, 416.2, and 324.31 kg/cm². In 1999, Stephan et al found that 1-day compressive strength of cement mortar containing 2.5% wt of Zn was lower than that of the control. However, afterwards the compressive strength of the cement mortar rose to higher values than those of the control and other Zn concentrations.

Table 4.35: Compressive strength of cement mortar with different concentration of Zn

Concentration of Zn (ppm)	Blaine (cm ² /g)	1 day (kg/cm ²)	7 days (kg/cm ²)	28 days (kg/cm ²)	Thai standard minimum value (7 days)	Thai standard minimum value (28 days)
Control	3,411	112.98	250.19	347.04	150	245
3,000	4,074	129.65	308.47	396.65	150	245
10,000	3,279	84.75	280.51	403.95	150	245
25,000	3,600	17.67	263.97	416.20	150	245
50,000	3,823	15.01	255.01	324.31	150	245

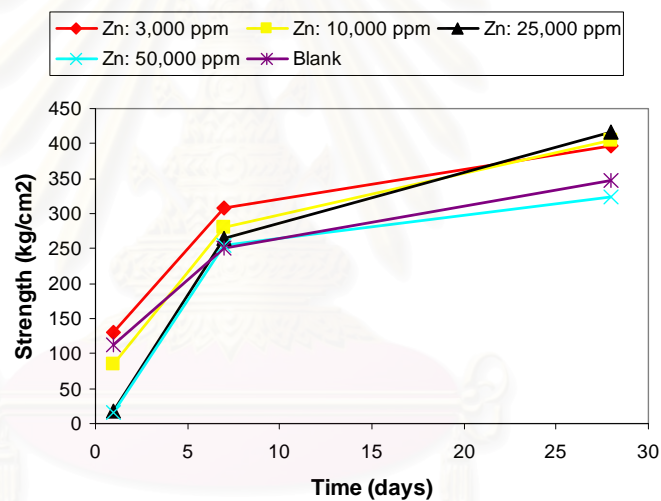


Figure 4.33: Compressive strengths of cement mortars with different Zn concentrations

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Chapter V

Conclusions

5.1 Conclusions

From the experimental results, it can be concluded that the 2.5% mixture of shale core and clay with raw meal produced a suitable condition for the burning process in the pilot-scale rotary cement kiln. The raw meal that contains high concentrations of Zn loss weight during loss on ignition test. Cr and Ni in the raw meal did not have an effect in the loss on ignition even though they increase concentrations of Ni and Cr in the raw meal. The suitable rotation speed for the burning process is 1 round per minute. The pilot scale rotary cement kiln was adjusted to position the raw meal closer to the burners. The thermocouple at the inlet part of the pilot-scale rotary cement kiln can measure the temperature. The pilot-scale rotary cement kiln was heated for around 3 hr., the raw meal was added at a temperature of 1,100°C, and it was burned for around 40 min. The effects of each of the three heavy metals in the clinker can be classified as follow:

A high concentration of Cr in the raw meal can increase the concentration of free lime. The free lime was higher when compared with the control. Cr prohibited transformation of C_2S to C_3S , thus producing clinker with lower C_3S . High concentration of Cr was also found to increase the LSF value. Cr gives a green color to the clinker. By using SEM analysis, it was determined that Cr usually was trapped into C_3S and C_2S . By using XRD, after the burning process, it was determined that Cr reacts with the chemical components to get Calcium aluminum chromium oxide ($Ca_6Al_4Cr_2O_{15}$). Cr was easily leached in the WET process when compared to the other two heavy metals. However, the WET values of the clinker with different ratios of Cr remained within the acceptable range according to the DIW standard. High concentrations of Cr in the cement mortar reduce compressive strength. With regard to Ni's effects on cement properties, the free lime content is reduced when the Ni concentration in the raw meal is increased.

At the 1.0 and 1.5% wt of Ni in clinker, the free lime content was lower than control. C_3S , C_3A , C_4AF of clinker with different ratio of Ni still quite similar, whereas, C_2S gradually decreased when the Ni concentration increased in clinker. Increased concentrations of Ni does not have an effect on the chemical oxides, SM, AM, and LSF in the clinker samples. Using SEM analysis, Ni was also found in C_3S and C_2S in the clinker phase. The results from XRD show that Ni reacted with Mg in the burning process and produced magnesium nickel oxide solution ($MgO \cdot 4NiO \cdot 6O$). Ni could not be detected by the WET. At day 28, the compressive strength of the cement mortar was increased due to the rise the Ni concentration in clinker. In addition, 1.0%wt of Ni in the cement mortar gave it higher compressive strength than that of the control.

In the study about effects of Zn on the cement phase, high concentrations of Zn in raw meal reduced the concentrations of free lime in the clinker. The free lime in clinker samples that contained Zn were also lower than that of the control. The utilization of 2.5% and 5.0% wt of Zn gave a very high concentration of C_2S . High concentration of

Zn, caused of overburned in clinker and the color of the clinker was light brown. Like Cr, high concentrations of Zn give high LSF values. All of the Cr, Ni, and Zn mixtures produced higher total heavy metal values in the clinker samples higher than the raw meal samples. 5.0% wt of Zn in the clinker sample created large sized of C_3S . However, it was difficult to indicate the other chemical minerals. MAD-10 Feldspar also found this sample to turn brown in color. By XRD analysis, it was determined that Zn reacted with iron, manganese, and chromium in the sample to get zinc iron manganese chromium oxide ($Zn [Fe_{0.5}Mn_{0.5}Cr] O_4$). Increased concentration of Zn in the clinker samples causes increased leaching behavior using the WET method. However, all of them were still within the acceptable limits of the DIW standards (B.E. 2548). On day 1 and day 7, high concentrations of Zn caused low level of compressive strength in the cement mortar, but by day 28, the Zn concentrations of 1.0% and 2.5% wt gave higher compressive strength values than the Zn concentration of 0.3 and 5.0% wt. When compared with the result of the control, 0.3, 1.0, and 5.0%wt of Zn in cement mortar produced high compressive strength performance. Delayed setting was the one cause of this situation. The cement mortar containing 2.5% wt of Zn gave the highest compressive strength when compared with samples that containing the other ratios of Zn.

5.2 Recommendations

1. The effects of heavy metals on setting time and percent residue using different sieves should be studied. Setting time and percent residue are related to the characteristics compressive strength. In addition, different thermal gravimetric test should be performed to study indicated the formation of heavy metals in the clinker phase under different temperature in the burning process.
2. Since the pilot-scale rotary cement kiln was controlled manually, problems occurred when it stopped rotating at very high temperatures. The pilot-scale rotary cement kiln should be repaired. The halting of the burning process caused a lost of materials and the incomplete formation of clinker. Moreover, it caused pieces of protected cement and steel slag to contaminate the clinker which could affect its physical and chemical properties due to the difficulty of separating them out. Therefore, finding an efficient way for removing (e.g. using some magnet to remove steel slag) remaining materials and steel slag is important for example
3. The effects of organic wastes in the cement properties should be studied because organic wastes can be used as alternative fuel and can affect cement properties.

REFERENCES

- Andrade, F.R.D., Maringolo, V., and Kihara, Y. 2002. Incorporation of V, Zn and Pb into the crystalline phases of Portland clinker. Journal of cement and concrete research 33: 63-71.
- 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. Spon press. Taylor and Francis group.
- Butt, M.Y., Timashev, V.V., and Malozohn, L.I. 1969. The crystallization of compounds in the presence of Cr₂O₃, P₂O₅ or SO₃ and the properties of the resultant cement, 5th ISCC. Suppl. Paper I-136, Tokyo: 340-347.
- 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 service.
- Espinosa, D.C.R., and Tenorio, J.A.S. 2000. Laboratory study of galvanic sludge's influence on the clinkerization process. Journal of Resource, Conservation, and Recycle. ELSEVIER: 71-82.
- 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 waste Management., 16: 295-303.
- Hewlett, P.C. 1998. Lea's Chemistry of Cement and Concrete, British cement association, UK
- Holcim, GTZ. 2006. Guildline on co-processing waste materials in cement production, The GTZ-Holcim Public Private Partnership.
- Kakali, G., and Parissakis, G. 1995. Investigation of the effect of zinc oxide on the formation of Portland cement clinker. Cem Concr Res 25: 79-85.
- Kasprzak, K.S, Sunderman Jr, F.W, and Salnikow, K. 2003. Nickel carcinogenesis. Journal of Mutation Research: 67-97.

- Knöfel, D. 1978. Beeinflussung einiger Eigenschaften des Portlandzementklinkers und des Portlandzementes durch ZnO und ZnS. Zement- Kalk-Gips 31: 157–161.
- Lemieux, P., Stewart, E., Realff, M., and Mulholland, J.M. 2003. Emissions study of co-firing waste carpet in a rotary kiln. Journal of environmental management, 27-33.
- Li, X.D., Zhang, Y.M., Poon, C.S., and Lo, I.M.C. 2001. Study of zinc in cementitious material stabilised/solidified wastes by sequential chemical extraction and microstructural analysis. Journal of Chemical Speciation and Bioavailability: 1-7.
- Mindess, S., Young, J.F., and Darwin, D. 2003. Concrete. 2nd ed. Prentice Hall.
- 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.
- Murat, M., and Sorrentino, F. 1996. Effect of large addition of Cd, Pb, Cr, and Zn to cement raw meal on the composition and the properties of the clinker and the cement. Cement and concrete research 26: 377-385
- Möller, A., and Jainski, J. 2008. Synthesis and Crystal Structure of AgCuVO₄. Journal of inorganic and general chemistry 10: 1669-1972
- 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.
- Older, I. 1990. Poly morphism and hydration of tricalcium silicate doped with ZnO. J.Am. Ceram. Soc. 66: 1-4.
- 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
- Phillips, B., and Muan, A. 1958. Phase equilibria in the system CaO- Iron oxide in air and at 1 atm. J. A. Cerem.Soc 4 (11): 445-454.
- Pollmann, H., Neubauer, J., König, U., and Monzet, H. 1997. Clinker quality using combined method- A study using microscopy and X- ray techniques- a study using combined methods-especially Reitveld method. Proc. 19th Int. Con. Cem.Micr. Cincinnati: 159-174.

- Portland Cement Association. 2001. Ettringite Formation and the Performance of Concrete. IS417, Portland Cement Association.
- Prawiro. 2003. The Design of a Data Acquisition (DAQ) System for a Rotary Kiln Incinerator, Louisiana State University: 1-28.
- React, P.G.; Espinosa, D.C.R.; and Tenorio, J.A.S. 2003. Determination of Cu and Ni incorporation ratios in Portland cement clinker. Journal of Waste management 23: 281-285.
- Rehmet, A., Lee, A., Goyal, A., and Mensinger, M.C. 1999. Construction-grade cement production from contaminated sediment using cement-lock technology, The Institute of Gas Technology (IGT): 1-11.
- Siam City Cement Public Co.LTD. 2008. The standard physical and chemical analysis of Cement: 1-2.
- Sorrentino, F.P. 1998. Dicalcium silicate in special cement. Proc. 20th Int. Conf. Cem. Micr, Guadalajara.
- Sprung S. 1985. Technological Problems in Pyroprocessing Cement Clinker: Cause and Solution. Du'' sseldorf: Beton.
- Stephan, D., Mallmann, D., Knofel, D., and Hardtl, R. 1999. High intakes of Cr, Zn, and Ni in clinker Part I Influence on burning process and formation of phase. Journal of cement and concrete research 29:1949-1957.
- Stephan, D., Mallmann, D., Knofel, D., and Hardtl, R. 1999. High intakes of Cr, Zn, and Ni in clinker Part II Influence on hydration properties. Journal of cement and concrete research 29: 1959-1967.
- Suvimol, A., Naksrichum, S., and Harnwajanawong, N. 2005. Strength, leachability and microstructure characteristics of cement-based solidified plating sludge. Cement and concrete research 35: 1042-1049
- Taylor, J.C. and Aldridge, L.P. 1994. Quantitative X-ray diffraction analysis of Portland cement. Proc.Int.Ceram.Conf.: 141-146.
- Taweekitwanit, E. 2004. Leaching behavior of heavy metal from cement derived form the co-burning of hazardous waste. Chulalongkorn University.
- Thai Industrial Standard Institute. 2002. TISI 15-2532.Thai Standard for Cement Industrial. Ministry of Industrial.
- Thai Standard. 2005. Elimination of hazardous and non-hazardous waste: 14-54.

Trezza, M.A., and Scian, A.N. 2000. Burning wastes as an industrial resource their effect on Portland cement clinker. Journal of cement and concrete research: 137-144.

US Environmental Protection Agency. 2006. Report to Congress on Cement Kiln Dust. Cement Industry Overview.

Welch, J.H.; and Gutt, W. 1959. Tricalcium silicate and its stability with in the system CaO-SiO₂. J.AM.Ceram.Soc 42: 11-15



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX A

The pilot-scale rotary cement kiln



Figure A-1 Pilot-scale rotary cement kiln



Figure A- 2 Pilot scale-rotary cement kiln was rose up to remove some residue



Figure A-3 Damage inside the pilot scale rotary cement kiln



Figure A-4 New casting protected heat cement inside the kiln and two burners



Figure A-5 Two blowers



Figure A-6 Cooling tower



Figure A-7 Air pump for control spray of the water in cooling tower



Figure A-8 Gas station and pressure control



Figure A-9 Stainless steel type 235 capsules for adding sample



Figure A-10 Control boxes



Figure A-11 Roller for moving the rotary kiln



Figure A-12 The 1 horse power of motor for driving the rotary kiln



Figure A-13 Thermocouple in the inlet part of the pilot-scale rotary cement kiln



Figure A-14 Adding sample process

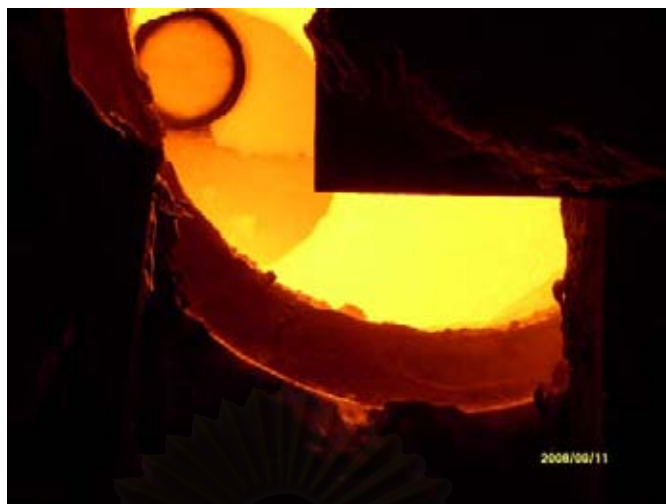


Figure A-15 Heating inside the rotary kin.



Figure A-16 Reparation of pilot-scale rotary cement kiln

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX B

The instruments for analyzing samples



Figure B-1 Mixing machine for mixing between each collected raw meal



Figure B-2 The V-mixed machine

สถาบันวิจัยและพัฒนา
จุฬาลงกรณ์มหาวิทยาลัย



Figure B-3 Swinging mill machine



Figure B-4 Tablet machine for using in the combination machine of XRF and XRD



Figure B-5 Combination machine of XRF and XRD



Figure B-6 Grinding machine for reducing size of clinker sample



Figure B-7 Compressive machine



Figure B-8 Specimen for compressive strength test

APPENDIX C

The raw material and results

Kiln feed

Table C-1: Average chemical compositions percentages of the kiln feed from silo numbers 5 and 6 of factory number 3

Chemical composition	Kiln feed from silo 5, factory number 3	Kiln feed from silo 6, factory number 3
SiO ₂ (%)	13.330	12.643
Al ₂ O ₃ (%)	2.892	3.010
Fe ₂ O ₃ (%)	2.036	2.052
CaO (%)	44.036	44.614
MgO (%)	1.060	0.929
K ₂ O (%)	0.310	0.335
Na ₂ O (%)	0.065	0.032
SO ₃ (%)	0.182	0.203
P ₂ O ₅ (%)	0.061	0.059
Cl (%)	0.013	0.011
LOI (%)	35.717	36.067
TiO ₂ (%)	0.146	0.144
Mn ₂ O ₃ (%)	0.036	0.036
SUM	99.883	99.984
LSF	104.764	110.809
SM	2.709	2.498
AM	1.401	1.468
Naeq (%)	0.269	0.251
BF	125.645	131.840

Table C-2 The chemical composition of shale core, clay, and mixture of shale core and clay (25 g: 20g)

Chemical composition	Shale core	Clay	Mixture of shale core an clay (25:20)
SiO ₂ (%)	76.170	35.207	57.864
Al ₂ O ₃ (%)	11.203	29.223	18.383
Fe ₂ O ₃ (%)	5.493	13.096	7.507
CaO (%)	3.674	1.214	3.714
MgO (%)	0.702	0.345	0.581
K ₂ O (%)	1.781	0.001	1.110
Na ₂ O (%)	0.085	0.001	0.005
SO ₃ (%)	0.156	0.028	0.120
P ₂ O ₅ (%)	0.068	0.068	0.085
Cl (%)	0.001	0.001	0.001
LOI (%)	3.649	1.329	3.549
TiO ₂ (%)	0.504	1.416	0.776
Mn ₂ O ₃ (%)	0.059	0.091	0.058
SUM	103.543	82.018	93.752
LSF	1.597	0.857	1.969
SM	4.562	0.832	2.235
AM	2.040	2.231	2.449
Naeq (%)	1.250	0.001	0.736
BF	41.123	8.126	20.224

Table C-3 Chemical composition of the kiln feed after the addition of a 2.5% mixture of shale core and clay

Chemical composition	Mixed kiln feed
SiO ₂ (%)	14.345
Al ₂ O ₃ (%)	3.290
Fe ₂ O ₃ (%)	2.302
CaO (%)	43.097
MgO (%)	0.965
K ₂ O (%)	0.336
Na ₂ O (%)	0.052
SO ₃ (%)	0.230
P ₂ O ₅ (%)	0.064
Cl (%)	0.012
LOI (%)	34.877
TiO ₂ (%)	0.162
Mn ₂ O ₃ (%)	0.037
SUM	99.780
LSF	94.570
SM	2.567
AM	1.429
Naeq (%)	0.274
BF	114.530



Figure C-1 The collection of kiln feed



Figure C-2 The 2.5% of mixture of shale core and clay

Clinker control

Table C-4 Composition of the control clinker after the dynamic process.

Chemical mineral	Concentration (%)
C ₃ S	64.410
C ₂ S	10.446
C ₃ A	7.616
C ₄ AF	10.247
Free lime	1.462

Table C-5 The concentration of chemical oxide, LSF, SM, and AM of clinker control.

Chemical oxides	Concentrations
SiO ₂	20.630
Al ₂ O ₃	5.770
Fe ₂ O ₃	3.053
CaO	66.551
LSF	95.405
SM	2.344
AM	1.890

Table C-6 Compressive strength of cement mortar control

Item	Quantity (g)	Blaine (cm ² /g)	1 day (kg/cm ²)	7 days (kg/cm ²)	28 days (kg/cm ²)
Control	800	3,411	112.98	250.19	347.04

**Figure C-3** Clinkers before cooling the temperature of them by air**Figure C-4** Clinkers control



Figure C-5 Clinker after crushed by the grinding machine



Figure C-6 Cement mortar control after compressed by the compressive machine

C.3 Chromium

Table C-7 Percent moisture contents of kiln feed contained different ratios of Cr

Concentration of Cr (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
5,000	0.12	0.12	0.10	0.11
10,000	0.10	0.10	0.06	0.09
25,000	0.10	0.10	0.10	0.10
50,000	0.10	0.12	0.06	0.09

Table C-8 Percent loss of weight of kiln feed during ignition contained different ratios of Cr

Concentration of Cr (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
5,000	4.88	5.20	4.92	5.00
10,000	5.76	4.62	5.58	5.32
25,000	5.46	4.78	4.92	5.05
50,000	5.61	4.91	5.55	5.36

Table C.9 Free lime in the clinker contained different concentrations of Cr

Sample (ppm)	Free CaO (%)
Cr : 5,000	1.635
Cr : 10,000	1.576
Cr : 25,000	1.826
Cr : 50,000	1.172

Table C-10 Analyzed chemical minerals in the clinker samples contained different concentrations of Cr by XRD

Clinker samples with different ratio of Cr (ppm)	Chemical minerals			
	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)
5,000	49.533	24.285	3.819	10.861
10,000	40.610	27.195	4.378	11.028
25,000	20.144	40.328	4.522	11.331
50,000	14.951	34.609	4.709	13.228

Table C-11 The concentration of chemical oxide, LSF, SM, and AM in the clinker samples at different ratios of Cr

Clinker samples (ppm)	Chemical oxides (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	LSF	SM	AM
Cr: 5,000	21.555	4.771	3.189	65.288	95.934	2.708	1.496
Cr: 10,000	20.578	4.795	3.162	64.278	98.384	2.586	1.516
Cr: 25,000	19.100	4.505	2.847	62.512	103.076	2.598	1.582
Cr: 50,000	16.309	4.085	2.473	58.199	111.718	2.487	1.652

Table C-12 Compressive strength of cement mortar with different ratios of Cr

Concentration of Cr (ppm)	Quantity (g)	Blaine (cm ² /g)	1 day (kg/cm ²)	7 days (kg/cm ²)	28 days (kg/cm ²)
5,000	800	3,582	131.02	246.75	342.08
10,000	800	3,537	52.81	150.04	222.09
25,000	800	3,604	29.86	110.22	185.03
50,000	800	3,169	3.09	25.42	90.31

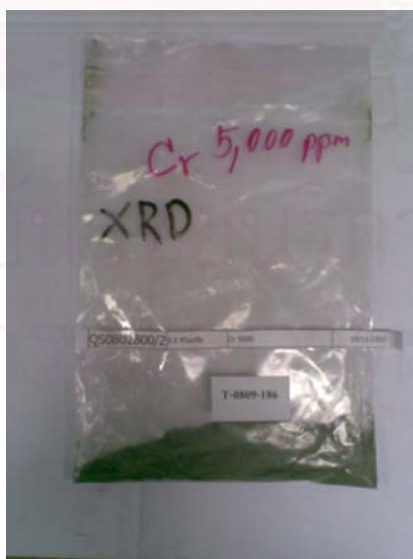


Figure C-7 Clinker contained 5,000 ppm of Cr

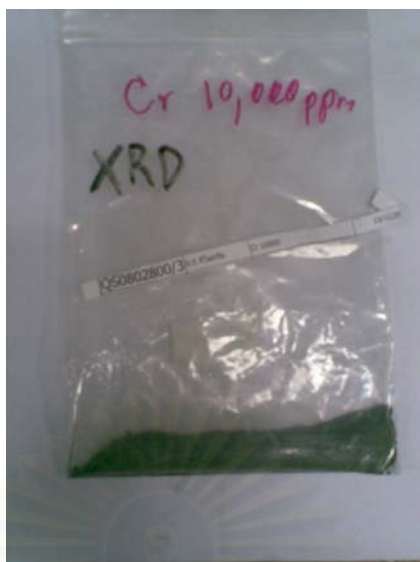


Figure C-8 Clinker contained 10,000 ppm of Cr

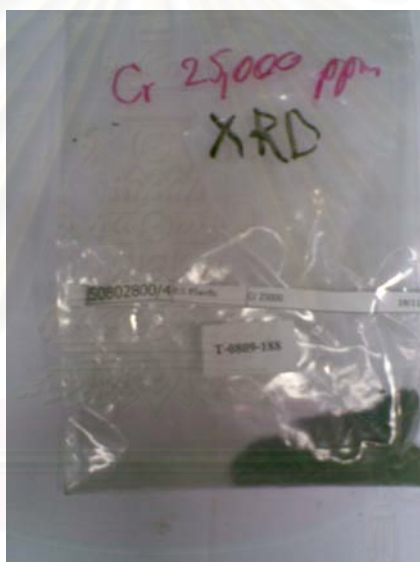


Figure C-9 Clinker contained 25,000 ppm of Cr

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Figure C-10 Clinker contained 50,000 ppm of Cr



Figure C-11 Green color of chromium (III) oxide

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Figure C-12 Bottle of chromium (III) oxide



Figure C-13 Mixture of kiln feed and chromium (III) oxide before mixing by V-mix machine

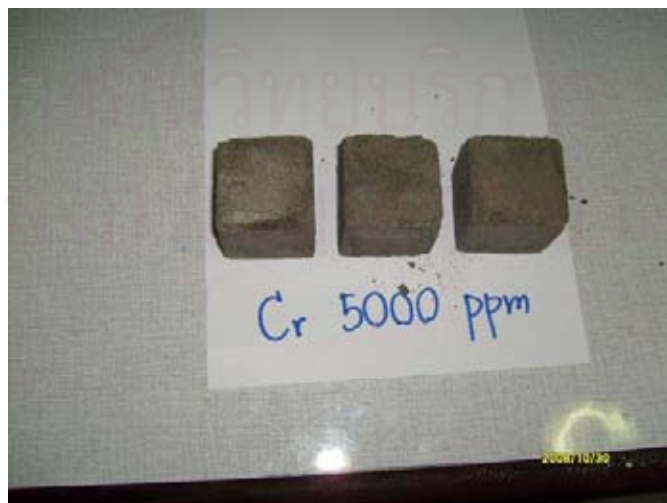


Figure C-14 Cement mortar contained 5,000 ppm of Cr



Figure C-15 Cement mortar contained 10,000 ppm of Cr



Figure C-16 Cement mortar contained 25,000 ppm of Cr



Figure C-17 Cement mortar contained 50,000 ppm of Cr

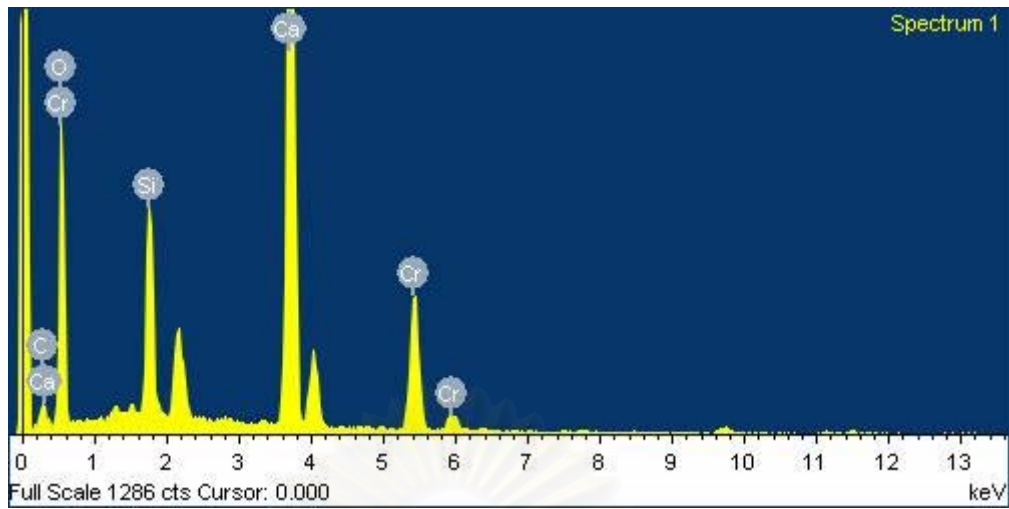


Figure C-18 Analysis of clinker phase (Cr: 50,000 ppm), Spectrum no.1 by SEM-EDS

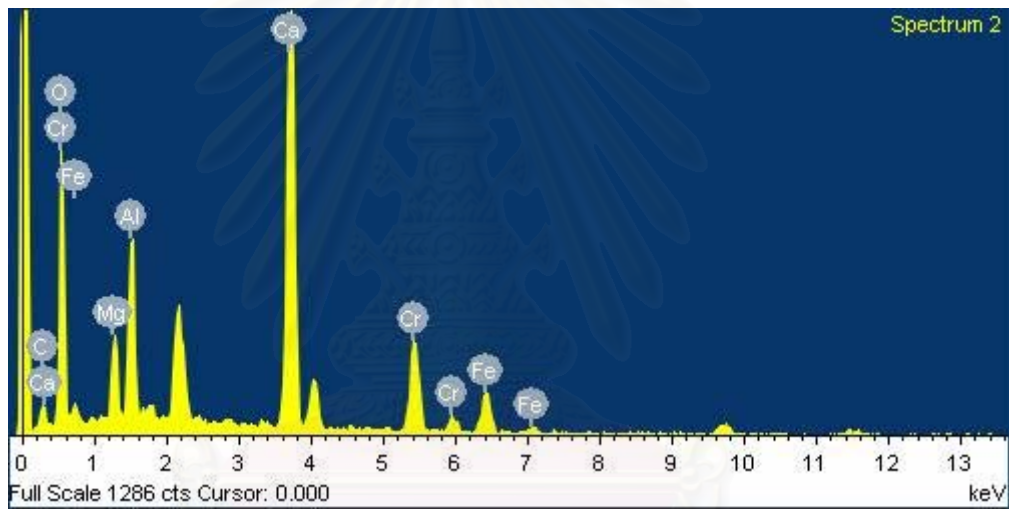


Figure C-19 Analysis of clinker phase (Cr: 50,000 ppm), Spectrum no.2 by SEM-EDS

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

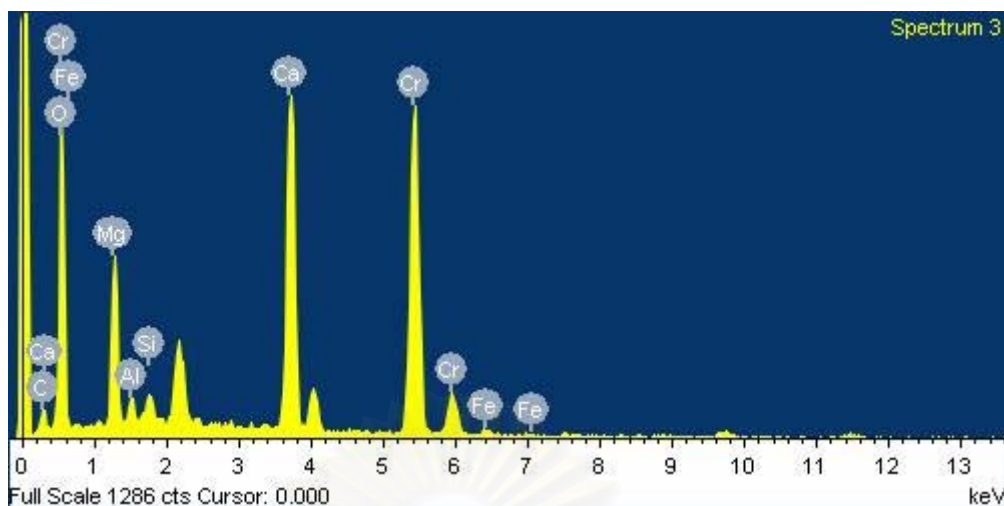


Figure C-20 Analysis of clinker phase (Cr: 50,000 ppm), Spectrum no.3 by SEM-EDS

C.4 Nickel

Table C-13 Percent moisture contents of kiln feed contained different ratios of Ni

Concentration of Ni (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
1,000	0.16	0.20	0.18	0.18
5,000	0.24	0.24	0.22	0.23
10,000	0.28	0.28	0.28	0.28
15,000	0.30	0.32	0.28	0.30

Table C-14 Percent loss of weight of kiln feed during ignition contained different ratios of Ni

Concentration of Ni (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
1,000	4.53	4.12	4.36	4.34
5,000	4.69	4.18	4.68	4.52
10,000	4.95	4.39	5.06	4.80
15,000	5.18	4.59	5.59	5.12

Table C-15 Free lime in the clinker contained different concentrations of Ni

Sample (ppm)	Free CaO (%)
Ni : 1,000	1.690
Ni : 5,000	1.630
Ni : 10,000	0.830
Ni : 15,000	1.010

Table C-16 Analyzed chemical minerals in the clinker samples contained different concentrations of Ni by XRD

Clinker samples with different ratio of Ni (ppm)	Chemical minerals			
	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)
1,000	62.350	15.840	8.180	10.910
5,000	62.230	14.960	7.980	10.940
10,000	62.090	13.680	8.130	10.910
15,000	61.290	13.430	7.960	10.970

Table C-17 The concentration of chemical oxide, LSF, SM, and AM in the clinker samples at different ratios of Ni

Clinker samples (ppm)	Chemical oxides (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	LSF	SM	AM
Ni: 1,000	21.930	5.380	3.590	66.430	94.780	2.440	1.500
Ni: 5,000	21.590	5.310	3.600	65.660	95.080	2.420	1.480
Ni: 10,000	21.110	5.360	3.590	64.810	95.640	2.360	1.490
Ni: 15,000	20.810	5.310	3.600	63.970	95.65	2.330	1.470

Table C-17 Compressive strength of cement mortar with different ratios of Ni

Concentration of Ni (ppm)	Quantity (g)	Blaine (cm ² /g)	1 day (kg/cm ²)	7 days (kg/cm ²)	28 days (kg/cm ²)
1,000	800	3,131	71.55	189.44	284.78
5,000	800	3,175	53.31	184.34	291.53
10,000	800	3,613	118.90	293.31	412.90
15,000	800	3,370	83.33	252.40	309.43

**Figure C-21** Clinker contained 1,000 ppm of Ni**Figure C-22** Clinker contained 5,000 ppm of Ni



Figure C-23 Clinker contained 10,000 ppm of Ni



Figure C-24 Clinker contained 15,000 ppm of Ni

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Figure C-25 Black color of nickel (II) oxide



Figure C-26 Bottle of nickel (II) oxide

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Figure C-27 The mixtures of kiln feeds and nickel (II) oxide before mixing by V-mix machine



Figure C-28 Cement mortar contained 1,000 ppm of Ni

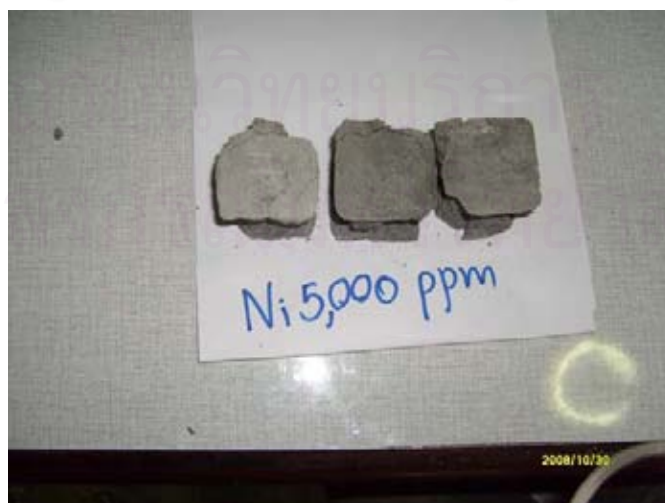


Figure C-29 Cement mortar contained 5,000 ppm of Ni



Figure C-30 Cement mortar contained 10,000 ppm of Ni



Figure C-31 Cement mortar contained 15,000 ppm of Ni

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

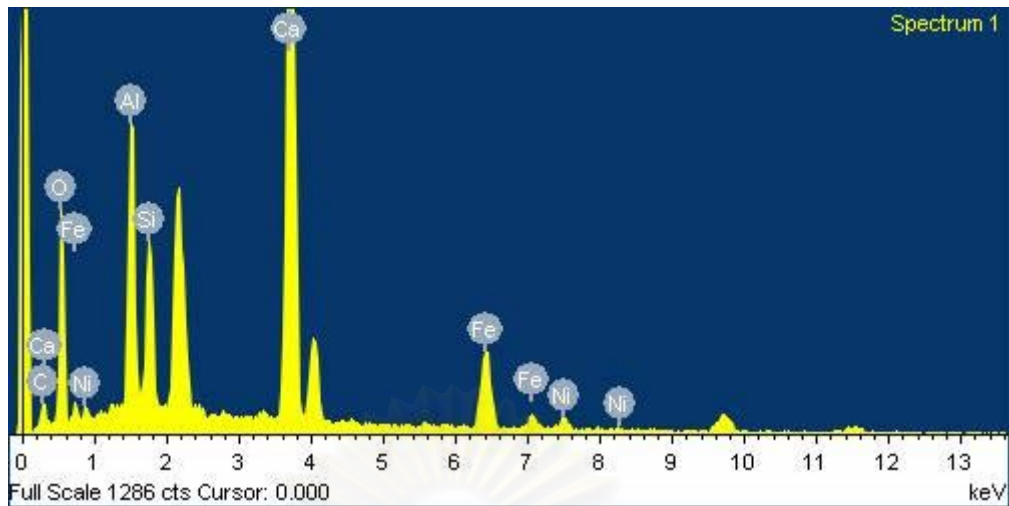


Figure C-32 Analysis of clinker phase (Ni: 15,000 ppm), Spectrum no.1 by SEM-EDS

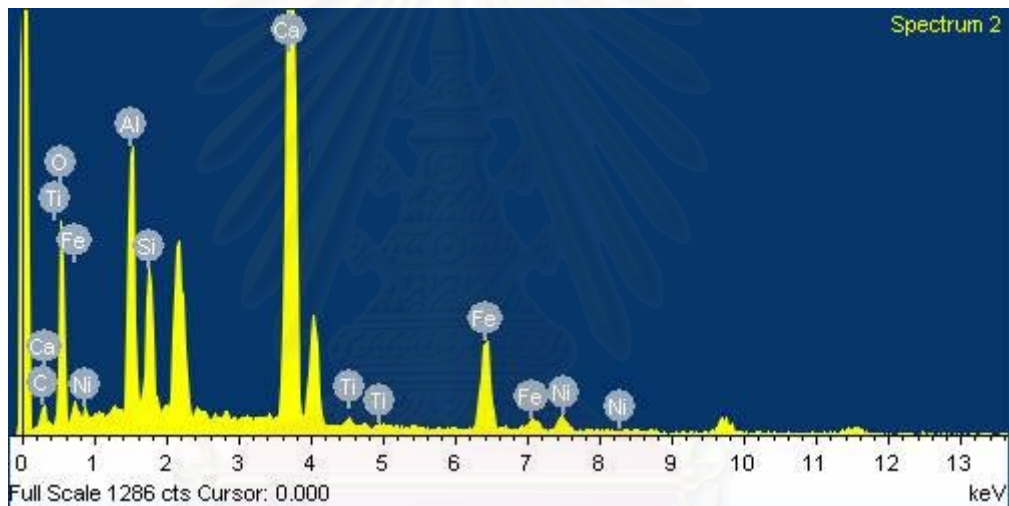


Figure C-33 Analysis of clinker phase (Ni: 15,000 ppm), Spectrum no.2 by SEM-EDS

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

C.5 Zinc

Table C-18 Percent moisture contents of kiln feed contained different ratios of Zn

Concentration of Zn (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
3,000	0.22	0.18	0.16	0.19
10,000	0.12	0.18	0.14	0.15
25,000	0.14	0.18	0.16	0.16
50,000	0.12	0.12	0.12	0.12

Table C-19 Percent loss of weight of kiln feed during ignition contained different ratios of Zn

Concentration of Zn (ppm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)
3,000	4.34	4.31	4.24	4.30
10,000	5.12	4.46	5.40	4.99
25,000	5.63	5.68	5.34	5.55
50,000	20.30	20.29	22.04	20.79

Table C-20 Free lime in the clinker contained different concentrations of Zn

Sample	Free CaO (%)
Zn: 3,000 ppm	1.293
Zn: 10,000 ppm	0.930
Zn: 25,000 ppm	0.604
Zn: 50,000 ppm	0.531

Table C-21 Analyzed chemical minerals in the clinker samples contained different concentrations of Zn by XRD

Clinker samples with different ratio of Zn (ppm)	Chemical minerals			
	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)
3,000	60.441	19.234	4.806	10.243
10,000	61.487	33.488	4.873	11.236
25,000	67.062	69.815	2.017	14.309
50,000	64.026	103.823	1.573	16.259

Table C-22 The concentration of chemical oxide, LSF, SM, and AM in the clinker samples at different ratios of Zn

Clinker samples (ppm)	Chemical oxides (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	LSF	SM	AM
Zn: 3,000	22.301	4.986	3.372	65.584	93.005	2.668	1.479
Zn: 10,000	21.546	5.420	3.349	64.569	93.722	2.460	1.618
Zn: 25,000	20.338	4.614	3.369	63.322	98.050	2.548	1.369
Zn: 50,000	17.560	4.166	3.471	60.055	106.596	2.299	1.200

Table C-23 Compressive strength of cement mortar with different ratios of Zn

Concentration of Zn (ppm)	Quantity (g)	Blaine (cm ² /g)	1 day (kg/cm ²)	7 days (kg/cm ²)	28 days (kg/cm ²)
3,000	800	4,074	129.65	308.47	396.65
10,000	800	3,279	84.75	280.51	403.95
25,000	800	3,600	17.67	263.97	416.20
50,000	800	3,823	15.01	255.01	324.31



Figure C-34 Clinker contained 3,000 ppm of Zn



Figure C-35 Clinker contained 10,000 ppm of Zn

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

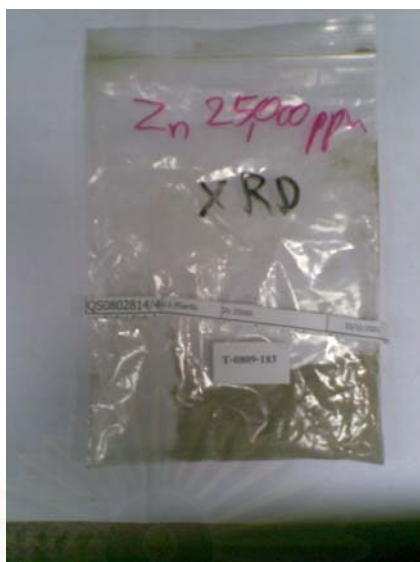


Figure C-36 Clinker contained 25,000 ppm of Zn



Figure C-37 White color of zinc oxide

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Figure C-38 The mixtures of kiln feeds and zinc oxide before mixing by V-mix machine

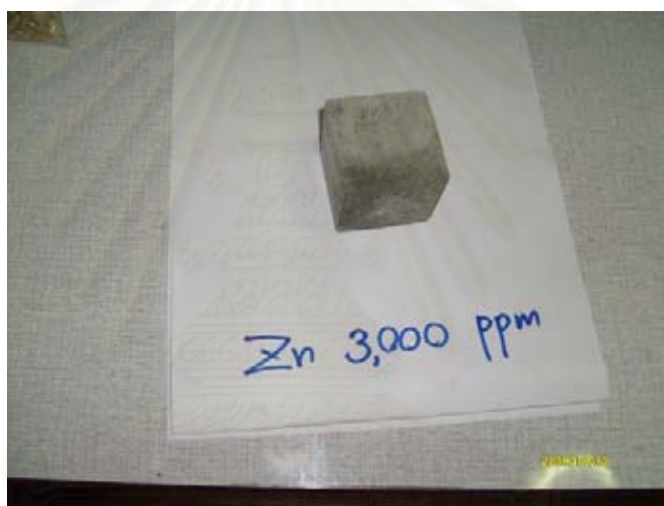


Figure C-39 Cement mortar contained 3,000 ppm of Zn

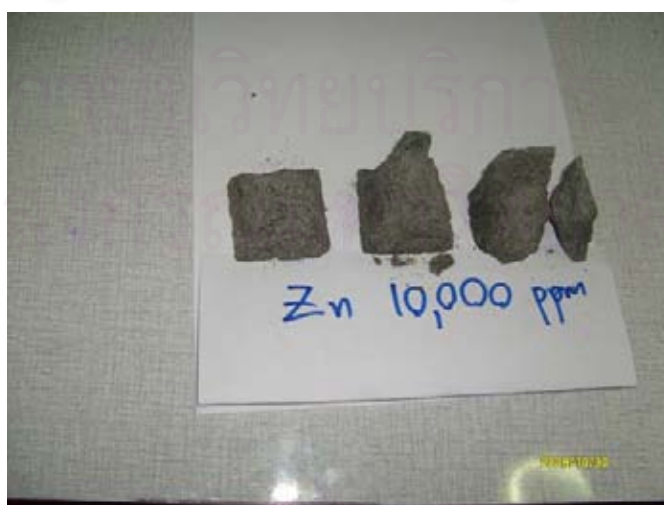


Figure C-40 Cement mortar contained 10,000 ppm of Zn

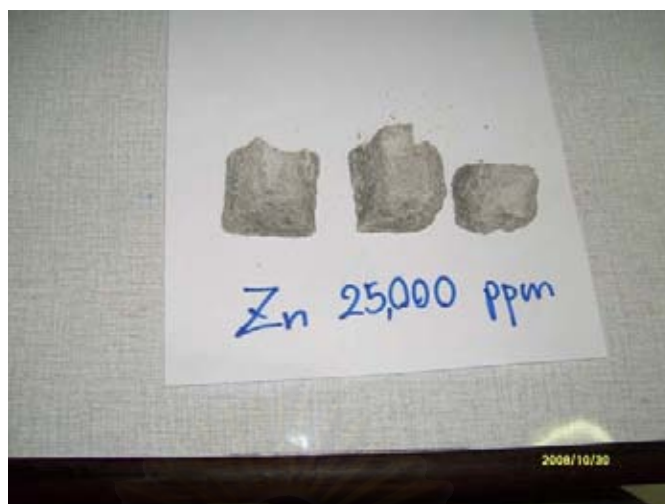


Figure C-41 Cement mortar contained 25,000 ppm of Zn



Figure C-42 Cement mortar contained 50,000 ppm of Zn

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

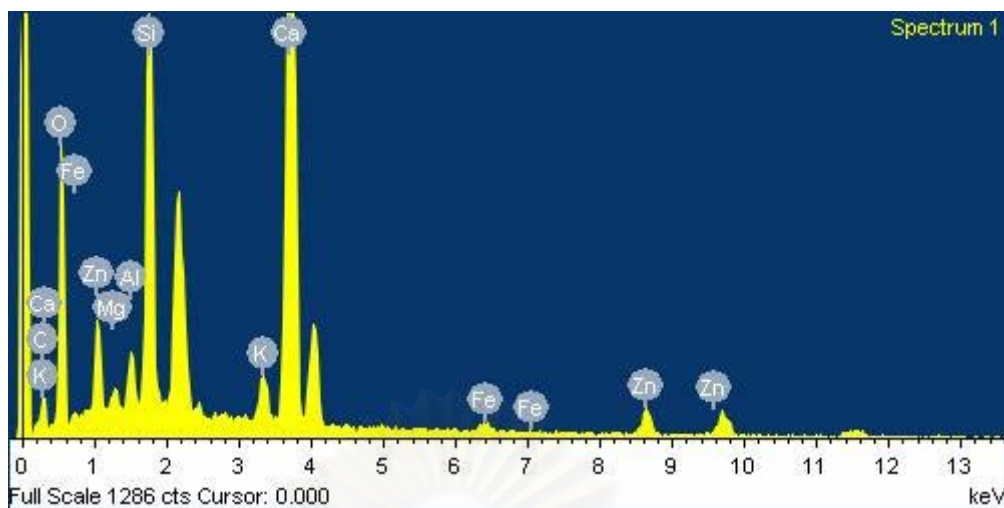


Figure C-43 Analysis of clinker phase (Zn: 50,000 ppm), Spectrum no.1 by SEM-EDS

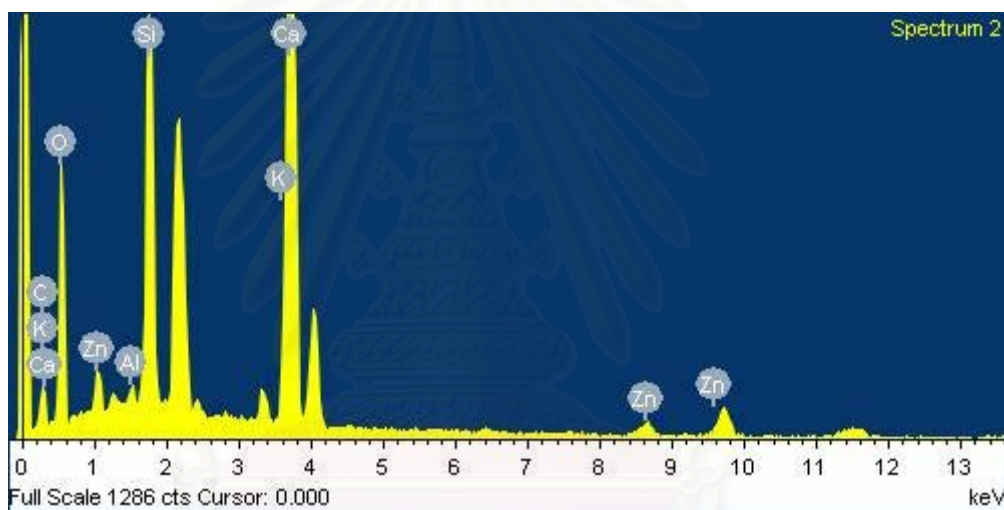


Figure C-44 Analysis of clinker phase (Zn: 50,000 ppm), Spectrum no.2 by SEM-EDS

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

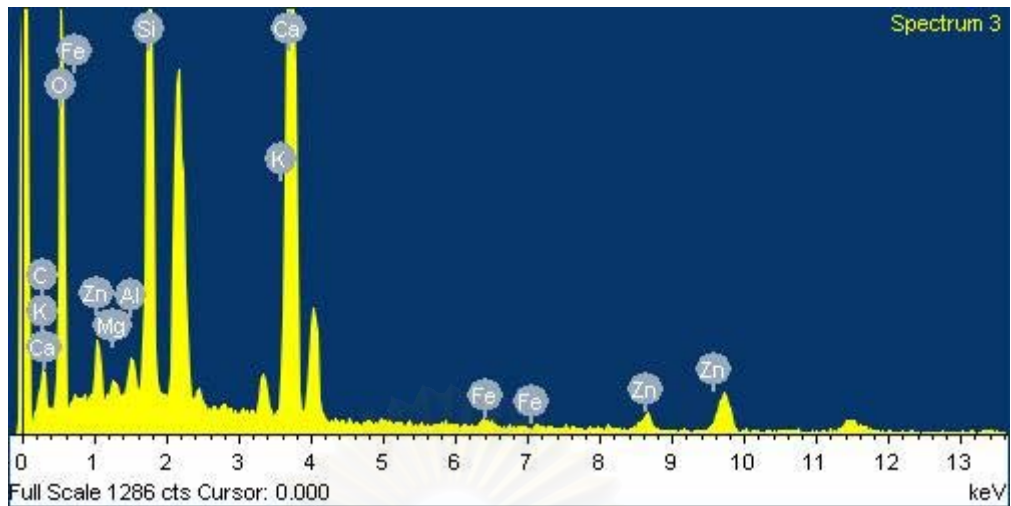


Figure C-45 Analysis of clinker phase (Zn: 50,000 ppm), Spectrum no.3 by SEM-EDS

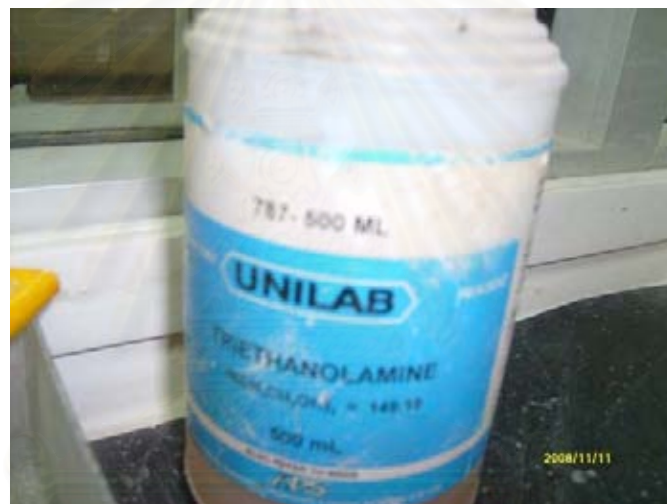


Figure C-46 Triethanolamine for using in XRF and XRD analysis

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

BIOGRAPHY

Name: Mr. Natt Dumkum

Date of Birth: March 22, 1984

Nationality: Thai

University Education: 2002-2005 Bachelor Degree of Environmental Management, Sirindhorn International Institute of Technology, Thammasart University, Phatumtani, Thailand

1990-2002 Graduated high school from Bangkok Christian Collage, Bangkok, Thailand

Presentation:

Manaskorn Rachakornkij, Viboon Sricharoenchaikul, Natt Dumkum, Jenwit Krobthong. *Physical and Chemical Characteristics of Cement Produced with Different Ratios of Zn, Cr, and Ni in Pilot-Scale Rotary Cement Kiln*. 12th International Conference on Integrated Diffuse Pollution Management (IWA DIPCON 2008). Research Center for Environmental and Hazardous Substance Management (EHSM), Khon Kaen University, Thailand; 25-29 August 2008.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย