

CHAPTER IV

RESULTS AND DISCUSSION



4.1 Optimum condition for clinker synthesis

In order to investigate the effect of heavy metal on synthesis clinker and use the obtained information to illustrate the leaching behavior of heavy metal from the real clinker, the synthetic clinker should be made with similar characteristic comparing with the real clinker. So, the optimum condition for clinker synthesis in laboratory must be found. The varied parameters for clinker synthesis were burning temperature and burning period. Analysis of free lime content, X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) were used to compare the characteristics of the real and the obtained clinkers.

The free lime content in the clinker is a good indicator of the burning. This value would decrease when CaO takes place in a reaction that leads to a new compound such as C_3S , C_2S , C_3A , and etc. Therefore, decreasing of free lime contents means an improvement in the burnability. In contrast a rising of free lime contents means deterioration in the burnability. XRD and SEM are used for structure analysis. The result from XRD shows the phases such as alite, belite, and aluminite of the clinker. The result from SEM shows the morphology of clinker such as the surface characteristic and the shape of each phases of clinker.

In this study, the interested burning temperature was in range 1,300-1,450°C which is the temperature for producing cement in manufacturing. Figure 4.1 shows the free lime content at different burning temperature. It was found that when the burning temperature increased, the free lime content decreased. In cement manufacturing process, the free lime content should be between 1 and 1.5%. In the studied temperature range, the lowest free lime content found at 1,450°C was 2.03%. The XRD was also used to compare the clinker characteristics between the obtained and the real clinkers.

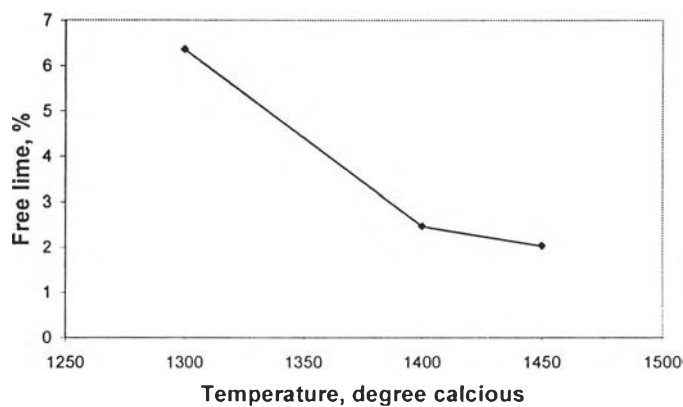


Figure 4.1 Free lime content as a function of burning temperature
(the burning time is 60 minutes)

Figure 4.2 shows the XRD spectrums at different temperatures. The prominent peaks in the clinker from industry were those of tricalcium silicate (C_3S) at 2θ of 29.5° , 32.6° , 33.8° , and 34.5° , dicalcium silicate (C_2S) at 2θ of 32.3° , 51.7° , 56.5° , and 62.2° and aluminite (C_3A) at 2θ of 38.8 . In comparison, the spectrums of all peaks obtained from the synthesis clinker are in the same position with those obtained from the real clinker in cement manufacturing process. The spectrum obtained from the synthetic clinker burning at $1,450^\circ\text{C}$ exhibited the most similar pattern as compared with spectrum of the real clinker. Thus, from this experiment set, the $1,450^\circ\text{C}$ is considered as the appropriate temperature for clinker synthesis. However, the burning period is required to investigate. It was expected that with the appropriate burning period, the spectrum of the synthetic clinker will be much more similar to the real clinker that can be used in the further experiments in this research.

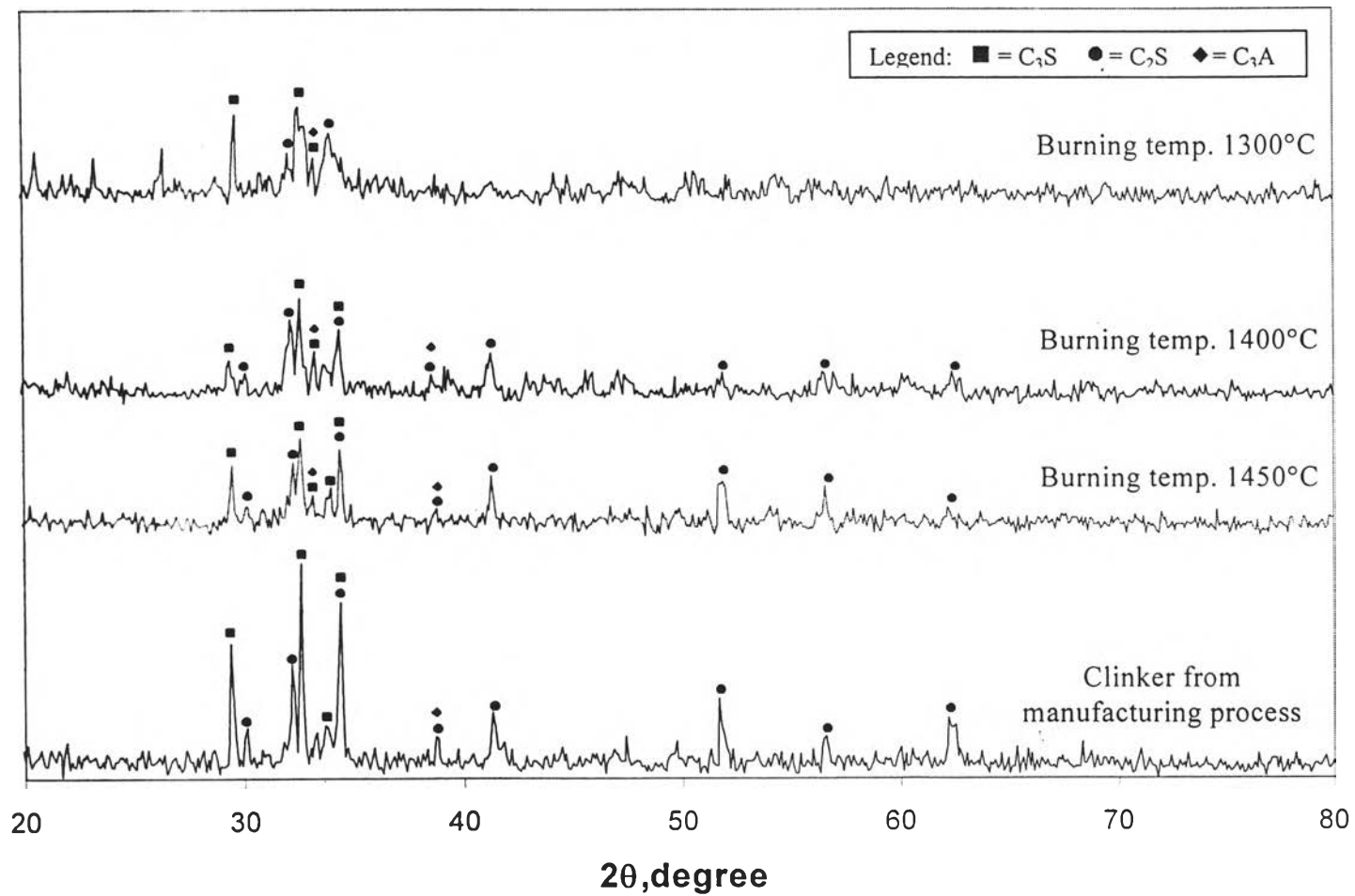


Figure 4.2 XRD patterns of clinker at different temperatures and clinker from industry

Figure 4.3 shows the content of free lime at different burning time. This test was performed at 1,450°C for all experimental conditions. It was found that the free lime content decreased, when the burning time increased. At 90 minute, the free lime was 1.21% and it is expected that the free lime content would be continuously reduced as the burning period is longer than 90 minutes. However, the free lime content at 90 minute of the burning period was in the acceptable range. Thus, the 90 minutes of the burning period was considered as an appropriate time for the further experiment sets.

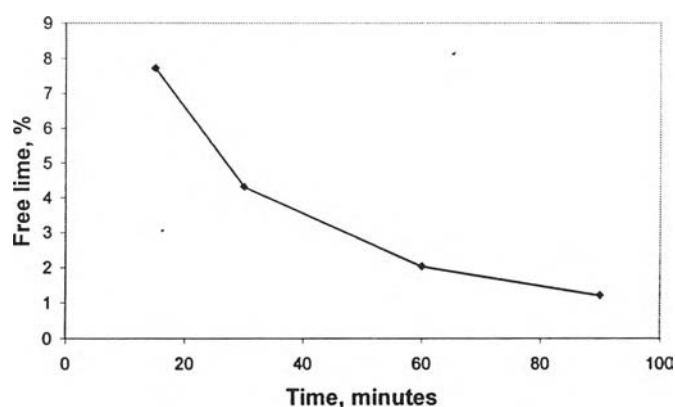


Figure 4.3 Free lime content as a function of burning time (All experiments conducted at 1,450°C burning temperature)

Figure 4.4 shows the structure analysis by XRD at different burning periods. The results show that the obtained clinker at 90 minute provided the similar prominent peak patterns as compared with those from the real clinker. With the XRD supporting data, the conditions to synthesis clinker at 1,450°C with 90 minutes burning period could be used as the optimum condition for clinker synthesis in the laboratory.

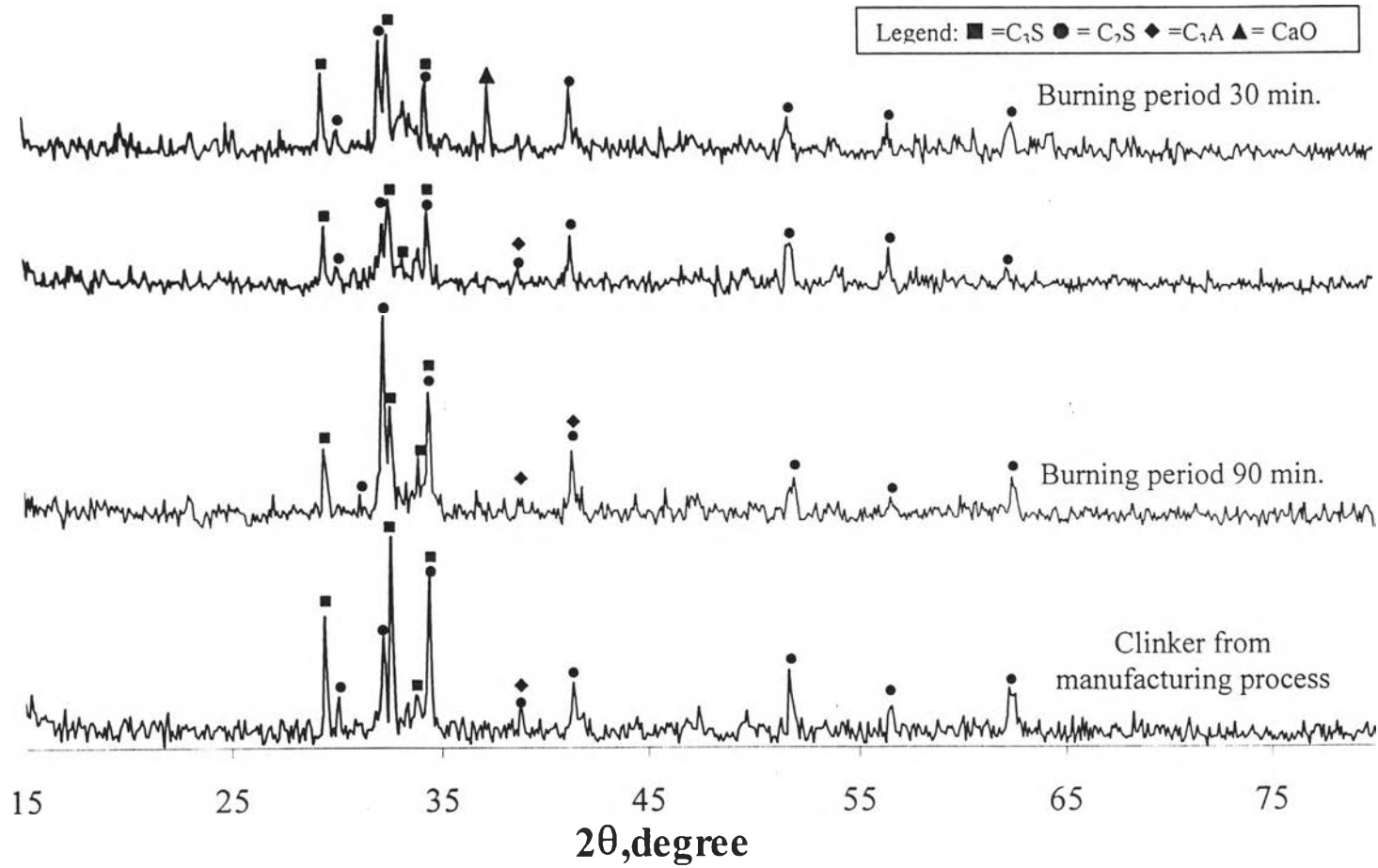


Figure 4.4 XRD patterns of clinkers at different burning periods and clinker from industry

Results of SEM were another evidences to support the similarity of synthesis and the real clinkers. Figure 4.5(a) and (c) show the morphology of clinker from industry that was analyzed at the magnification of 350 and 1,300, respectively. Figure 4.5(b) and (d) show the morphology of obtained clinker that was analyzed at the magnification of 350 and 1,300, respectively. It is obvious that the obtained clinker exhibited the similar morphology as compared to the real clinker.

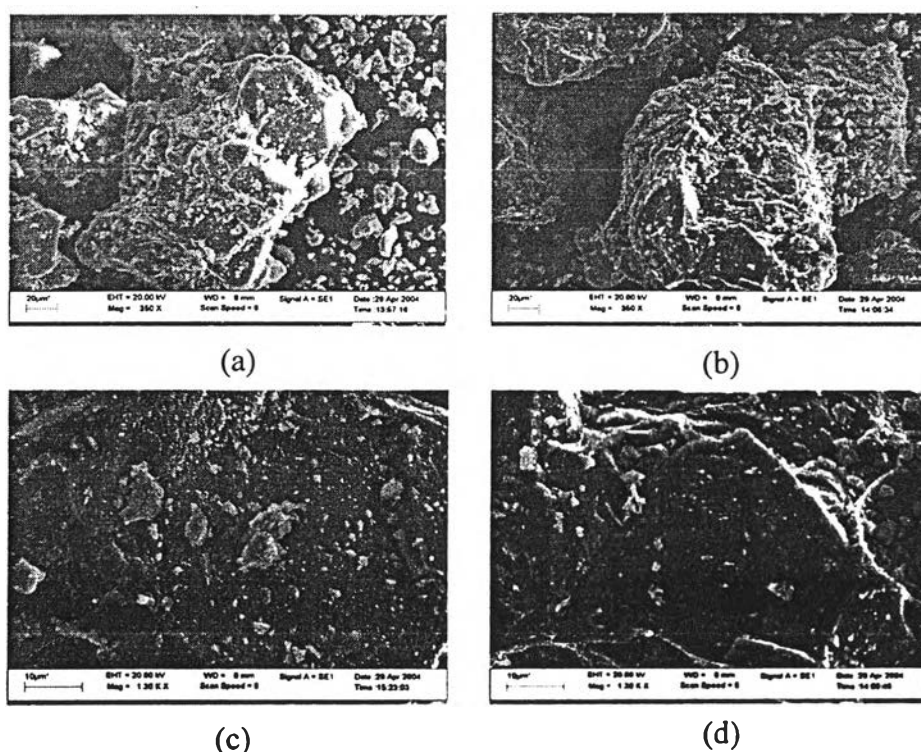


Figure 4.5 Phase analysis by SEM (a) clinker from industry 350x (b) simulated clinker 350x (c) clinker from industry 1,300x (d) simulated clinker 1,300X

Shapes of major phases of manufacturing clinker in this study were shown in Figure 4.6. Alite has a large size and its shape like a crystal. Belite is smaller than alite and it has a round shape. Aluminite is smaller than belite and it has a bar shape. Due to the small amount of C_4AF , the shape of this phase was not found in this study (Jourlin et al., 2001).

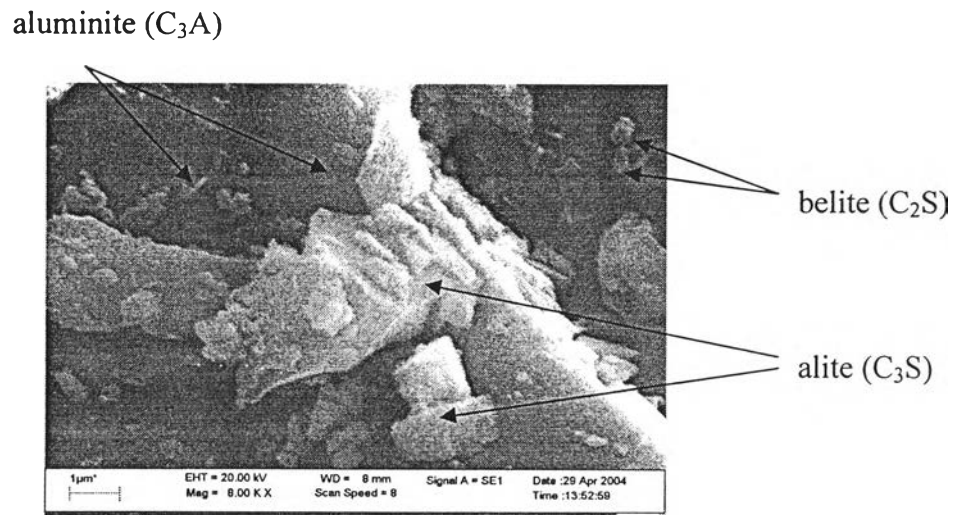


Figure 4.6 Shape of major phases of clinker

4.1 Effect of heavy metal on free lime

Figure 4.7 shows the free lime content at different of chromium concentrations. As the concentration of chromium less than 1.0 wt.% (according to the total weight of sample), the free lime content was change from 1.21% to 1.31%. When the concentration of chromium increase to 2 wt.%, the free lime content was increased as equal to 4.005%. Some effects of the chromium on the free lime content in clinker were described by previous researches. Malozhon et.al found a concentration of 1.5 wt.% of Cr_2O_3 in the sample, the content of free lime rose extremely. They also found a lower content of C_3S in clinker when doped with chromium. This effect was result from decomposition of C_3S . Stephan et.al also found the same results. Up to a concentration of 0.5 wt.% of chromium, the content of free lime decreased. Between 0.5 and 2.5 wt.%, the doping with chromium led to a high concentration of free lime. At 2.5 wt.% of chromium, the content of belite was always higher than that of alite. In addition, due to alite is formed by the reaction between belite and CaO. When chromium presented in the raw material, chromium would inhibit the reaction between belite and CaO to form alite (Stephan et al., 1999).

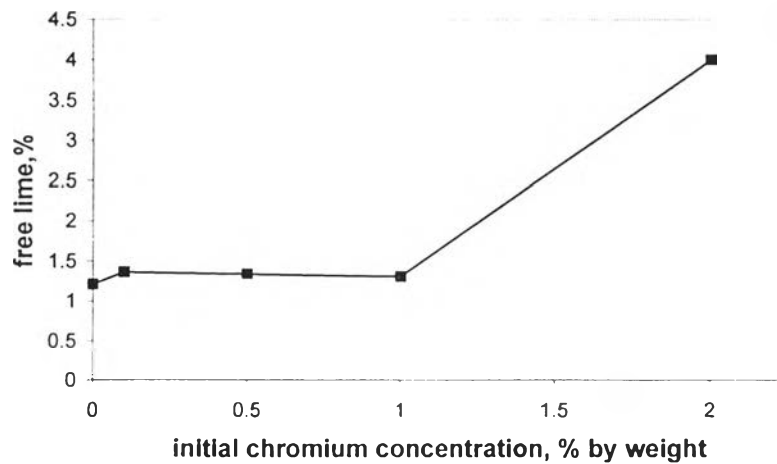


Figure 4.7 Free lime content of clinker doped with chromium

Figure 4.8 shows the free lime content at different of nickel concentration. The results show that the content of free lime decreased, as the concentration of nickel was increased from 0 to 2 wt.%. At 2 wt.% of nickel, the free lime was 0.64%. Stephan et.al. found that clinker with nickel showed a permanent decrease in the content of free lime.

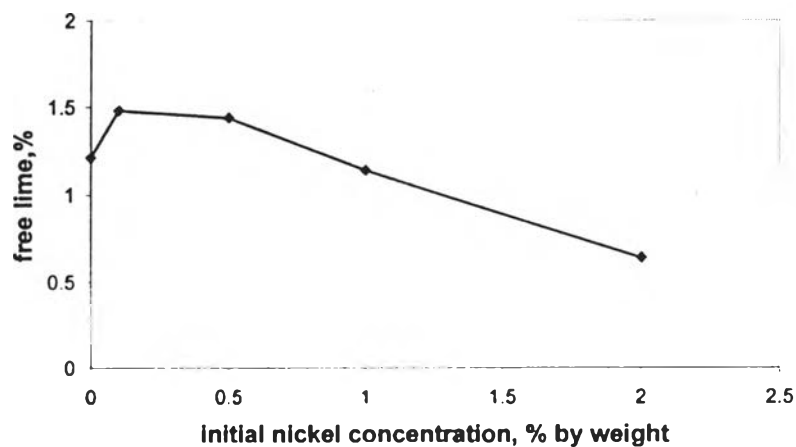


Figure 4.8 Value of free lime content of clinker doped with nickel

Figure 4.9 shows the free lime content at different of zinc concentrations. The results show that the free lime content decreased, when the concentrations of zinc increased from 0 to 2 wt.%. At 2 wt.% of zinc, the free lime content was 0.365%. Many previous studies investigated the effects of the zinc in clinker. Odler et al. as

well as Bordoloi et al. found a better burnability of clinkers containing zinc. Stephan et al. found that clinker with zinc showed a permanent decrease in the content of free lime. They also found that 2.5 wt.% of zinc showed a small increase of alite. Odler et al. interpreted the increasing of alite as due to a substitution of zinc for Ca. This free lime can react with belite to give more alite. Kakali and Parissakis found a new phase in the clinker containing more than 1.5 wt.% ZnO. The new phase was $2\text{CaO}\cdot\text{ZnO}\cdot\text{SiO}_2$.

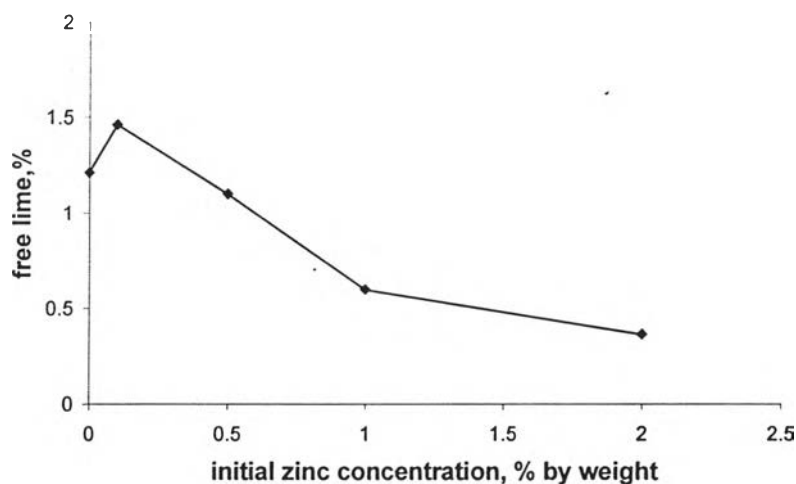


Figure 4.9 Free lime content of clinker doped with zinc

4.3 Leaching behavior of chromium

Figure 4.10 shows the results obtained from Microwave-assisted leach method 3051A. This result shows the total extracted concentration of chromium without chromium in siliceous matrices of cement for different initial concentrations of chromium. In the M3051A, a concentrated HNO_3 in a combination with heat was used to extract chromium from cement. However, some of the chromium were captured in the matrix of cement. Thus, the result from this test was a representative value of the total extracted concentration of heavy metal without heavy metal in siliceous matrices. From the result, it was shown that total extracted concentration of chromium without chromium in siliceous matrices is a function of initial concentration of chromium. As initial concentrations of chromium increased, total extracted of chromium was increased. The amounts of chromium detected from 0.1,

0.5, 1, and 2 wt.% of initial concentrations of chromium were 317.3, 1,531.3, 3,551.33, and 6,208.67 mg/kg, respectively.

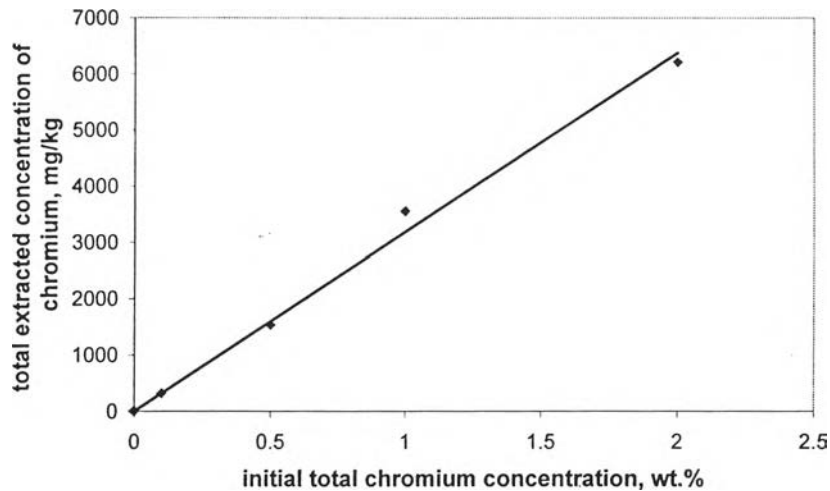


Figure 4.10 Average extracted concentration of chromium from M3051A

Figure 4.11 shows the results obtained from microwave assisted acid digestion of siliceous and organically based matrix method 3052. The concentrated HF in the combination with concentrated HNO_3 and heat was used to extract the chromium from cement. These tested conditions could destroy the siliceous matrix in the cement. Therefore, chromium in the matrix would be leached out. Results from the M3052 can be representative values of the total chromium in the cement. As can be seen in Figure 4.11, total chromium measured by M3052 is directly proportional to the initial total concentration of chromium. The amounts of chromium detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of chromium were 354, 1,753.33, 3,929, and 6,442 mg/kg, respectively.

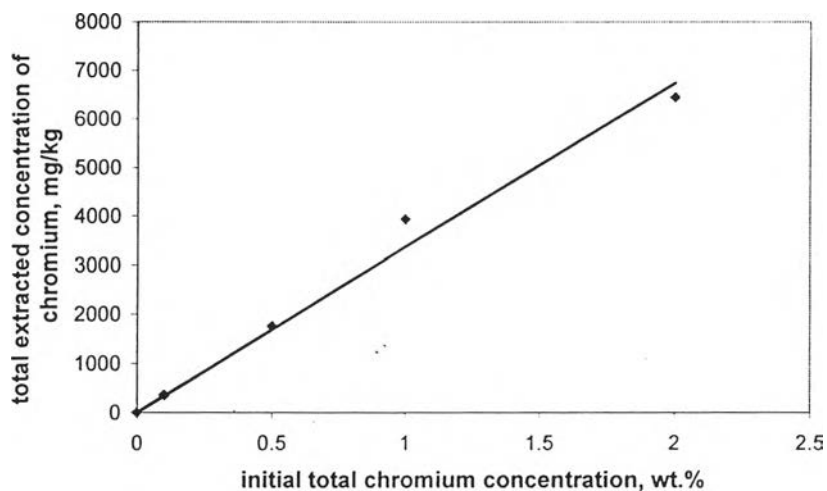


Figure 4.11 Average extracted concentration of chromium from M3052

Figure 4.12 shows the results obtained from availability leaching test (NEN 7341). The results show the maximum concentrations of chromium to be leached out at the extreme environmental conditions for different initial chromium concentrations. The results show that this value is a function of initial concentration of chromium. As initial concentration of chromium increased, maximum concentration of chromium to be leached out to environment increased. The amounts of chromium detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of chromium were 267.4, 1,368.6, 3,239, and 5,298 mg/kg, respectively.

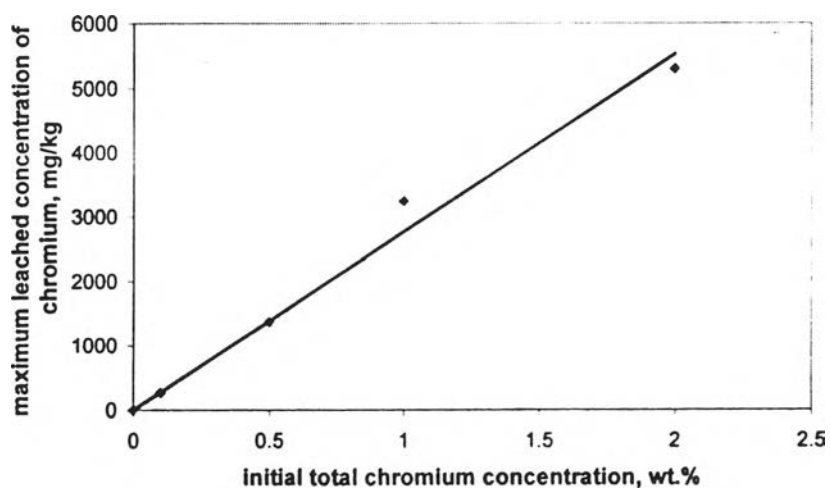


Figure 4.12 Average leached concentration of chromium from AVLT

Figure 4.13 shows the chromium concentration that leached from obtained cement using different test methods which were AVL, M3051A and M3052. As comparing the results between M3051A and M3052, it was found that most of chromium in clinker ready to leach out from cement was not fixed by siliceous matrices of cement. When the results of M3051A were taken to compare with AVL, it has been seen that the maximum concentrations of chromium to be leached out at the extreme environmental conditions was approximately 84.27-91.2%. On the basis of AVL as described earlier, it could be indicated that chromium was likely to be leached from the cement. In addition, with the suitable condition for leaching, most of chromium can be leached out from the cement.

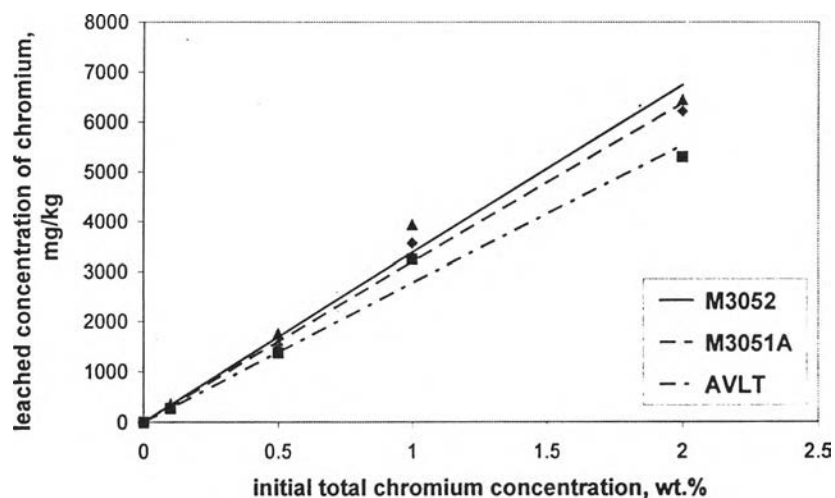


Figure 4.13 Comparison of M3052, M3051A, and AVL

This leaching behavior of chromium might be the result of the new phases formation of chromium compound in cement. From the XRD supporting data, as shown in Figure 4.14, it was found that the new phase of chromium was K_2CrO_4 . It is chromium with the valance of +6, which is readily soluble. Therefore, this compound might be the reason for the ease of leachability of chromium from cement. Some previous studies also indicated the new phases formation when chromium was doped in raw material. Stephan et al., 1999 reported that in the clinker containing with chromium and high concentrations of K, K_2CrO_4 and/or $K_2Cr_2O_7$ was found. Moreover, they also found the new phase as $Ca_4Al_6O_{12}Cr_4$, when added Chromium in pure raw material of clinker phase.

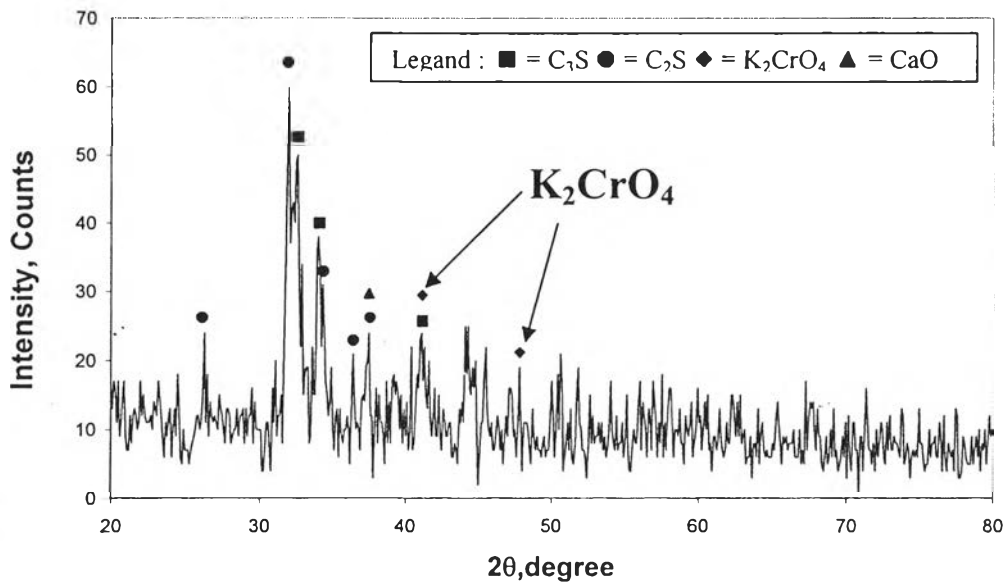


Figure 4.14 XRD patterns of clinker doped with chromium

Figure 4.15 shows the effects of pH and initial concentration of chromium on leaching behavior. From the graph, pH in the range of 4-10 had a few effect on the leachability of chromium, the leached concentrations of chromium were not significantly different. In comparison between the leached concentration of chromium and initial concentration of chromium for each conditions, it was found that the leached concentrations of chromium for pH in the range of 4-10 were approximately 17-20% of initial concentrations of chromium. It could be indicated that as the cement contaminated with chromium was used and contacted with water under various pH conditions, the maximum amount of chromium could be leached out approximately 20%. At pH 12, concentrations of chromium in the leachate were measured in less amount. From the previous study, the leachability of chromium was decreased at alkaline pH (van der Sloot, 2002). The previous studies found that less amount of chromium could be leached out with the pH higher than pH 8 (Serclerat et al., 2000; Wang and Vipulanandan, 2000). This might be result from the leaching behavior of K_2CrO_4 that is effectively leached out at weak acid or neutral pH. Beside, Wang and Vipulanandan, 2000 also reported that $CaCrO_4$ was found under alkaline pH conditions. The solubility of this new phase is very low which is 5.1×10^{-6} (CRC Handbook, 1996). The low solubility of this new phase might be a reason for the low concentration of chromium under alkaline pH conditions of this work.

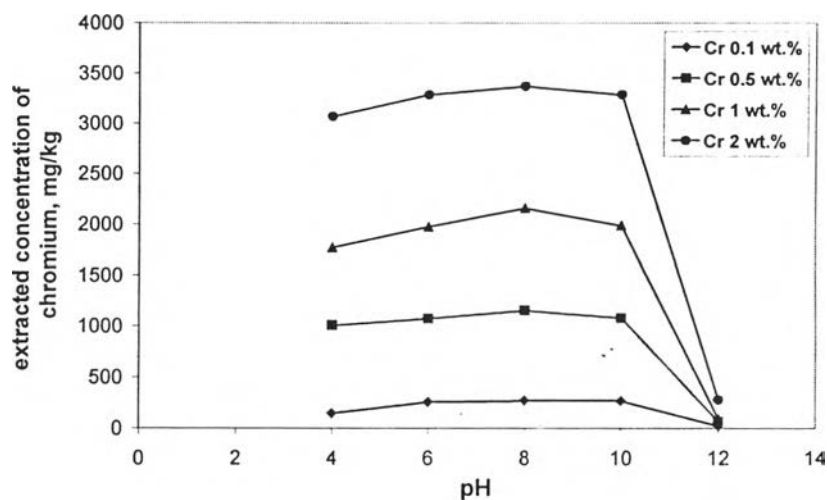


Figure 4.15 Average leached concentration from pH static leach test

After burning raw material containing chromium, most of chromium were remained in the clinker. When this clinker was used for cement production, this cement might be classified as hazardous waste. TCLP test and NFMI were employed in order to identify this cement as hazardous waste. Both tests were proposed by U.S. EPA and Thailand regulation, respectively. The results from TCLP were shown in Figure 4.16. It was found that leached concentrations of chromium is direct proportional to initial concentrations of chromium. After 18 hours of leaching, the amounts of chromium detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of chromium before burning process were 5.67, 26.34, 46.66, and 105.48 mg/l, respectively. According to the U.S. EPA, the allowable of chromium in leachate should be less than 5 mg/l. From the result, it has been seen that chromium in the extraction fluid was higher than the allowable value. Therefore, the raw material of cement doped with initial concentrations of chromium more than 0.1 wt.% could be identified as hazardous waste that can not be used as a product.

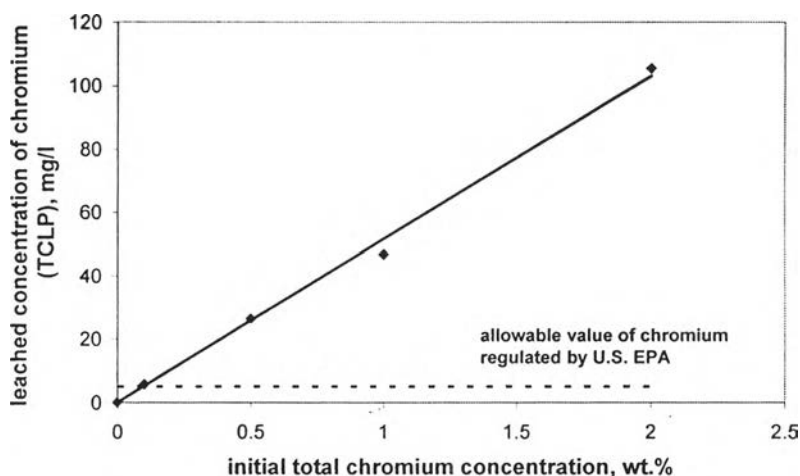


Figure 4.16 Average leached concentration of chromium from TCLP

Figure 4.17 shows the results obtained from NFMI. After 18 hours of leaching, the amounts of chromium detected from 0.1, 0.5, 1, and 2 wt.% of initial concentration of chromium were 5.26, 17.02, 28.28, and 40.28 mg/l, respectively. According to the Notification of Ministry of Industry No.6 B.E. 2540, the allowable of chromium in the leachate should be less than 5 mg/l. From the result, it has been seen that chromium in the extraction fluid was higher than the allowable value. Thus, the raw material of cement doped with initial concentration of chromium more than 0.1 wt.% could be identified as hazardous waste and can not be used as a product. As considering the results between TCLP and NFMI, the results from TCLP were agreed with NFMI that is the raw material of cement doped with initial concentration of chromium more than 0.1 wt.% could be classified as hazardous waste.

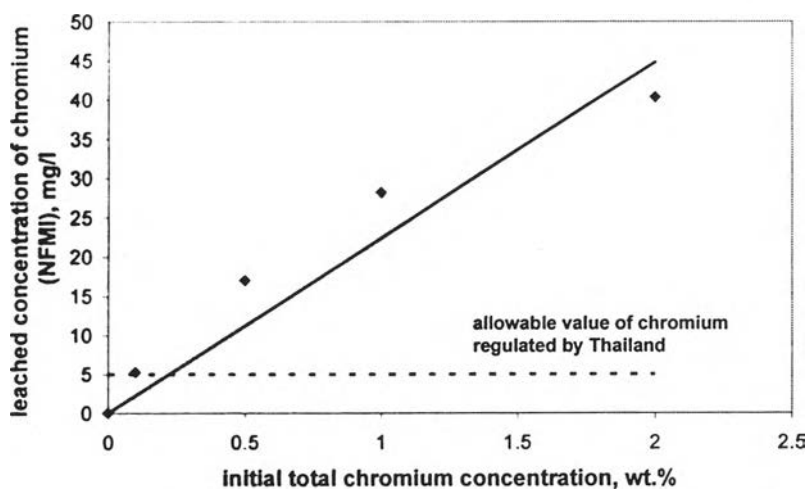


Figure 4.17 Average leached concentration of chromium from NFMI

4.2 Leaching behavior of nickel

Figure 4.18 shows the results obtained from Microwave-assisted leach method 3051A. From the graph, it was shown that total extracted concentration of nickel without nickel in siliceous matrices is a function of initial concentration of nickel. As initial concentration of nickel increased, extracted concentration of nickel increased. The amounts of nickel detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of nickel were 225.67, 860, 2430, and 4473.33 mg/kg, respectively.

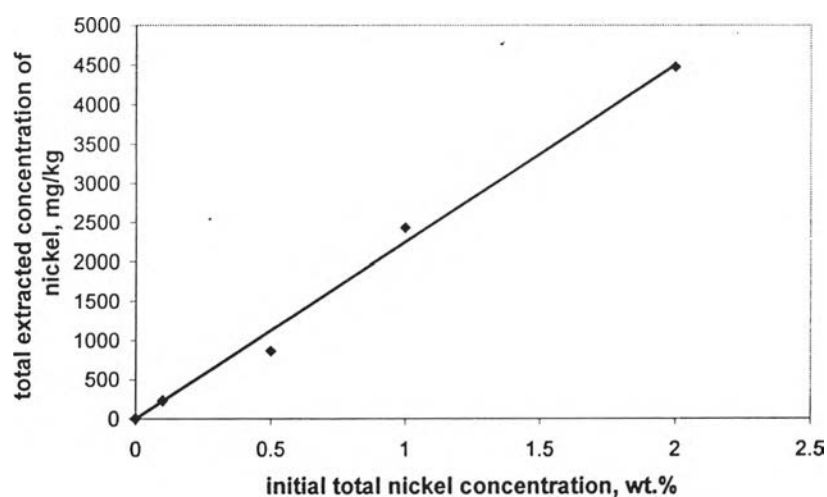


Figure 4.18 Average extracted concentration of nickel from M3051A

Figure 4.19 shows the results obtained from M3052. From the graph, it was found that total nickel is direct proportional to initial concentration of nickel. The amounts of nickel detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of nickel were 249, 1078, 2479, and 4596.3 mg/kg, respectively.

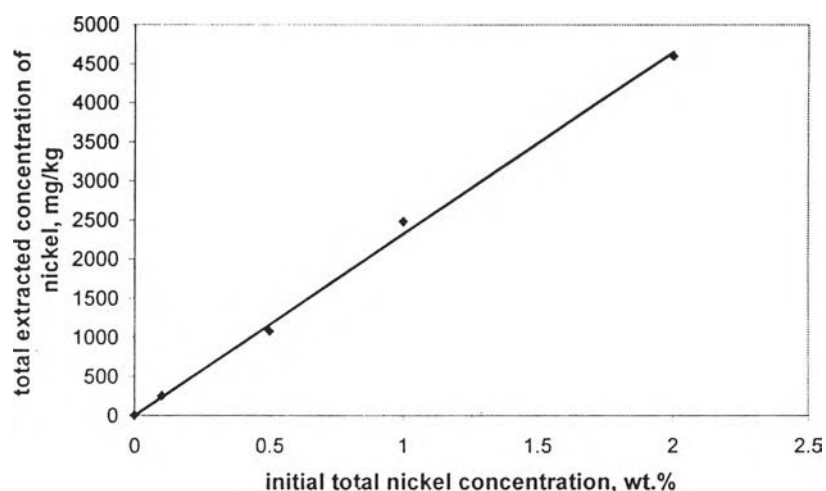


Figure 4.19 Average extracted concentration of nickel by M3052

Figure 4.20 shows the results obtained from availability leaching test (NEN 7341). The results show the maximum concentrations of nickel to be leached out at the extreme environmental conditions for different initial concentrations. From the graph, it was found that the maximum concentration of nickel is a function of initial concentration of nickel. As initial concentration of nickel increased, maximum concentration of nickel to be leached out at the extreme environmental conditions increased. The amounts of nickel detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of nickel were 6.66, 61, 146.7, and 311.5 mg/kg.

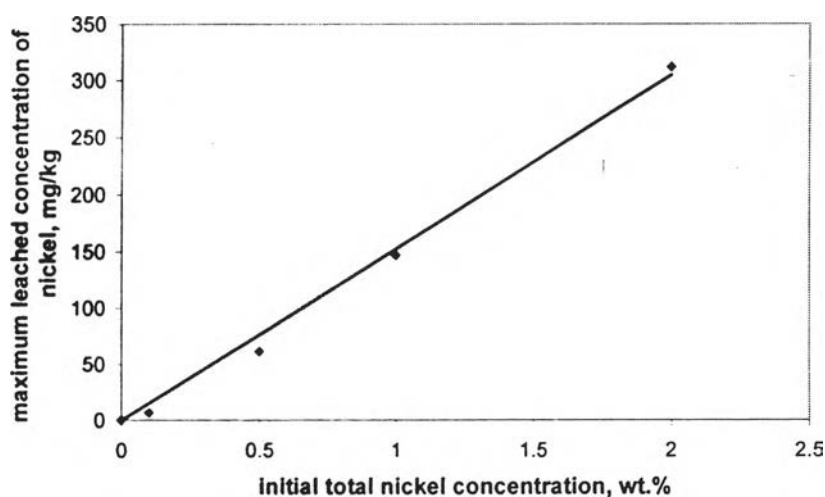


Figure 4.20 Average leached concentration of nickel by AVL T

Figure 4.21 shows the nickel concentration that leached from obtained cement using different test methods which were AVL, M3051A and M3052. As comparing the results between M3051A and M3052, most of nickel in clinker that ready to leach out from cement was not fixed by siliceous matrices of cement. When the results from M3051A were taken to compare with AVL, it has been seen that the maximum concentrations of nickel to be leached out at the extreme environmental conditions was approximately 2.95-7.09%. On the basis of AVL as described earlier, it could be indicated that nickel was unlikely to be leached from the cement. In addition, with the suitable conditions for leaching, there is a few of nickel in soluble form can be leached out from cement.

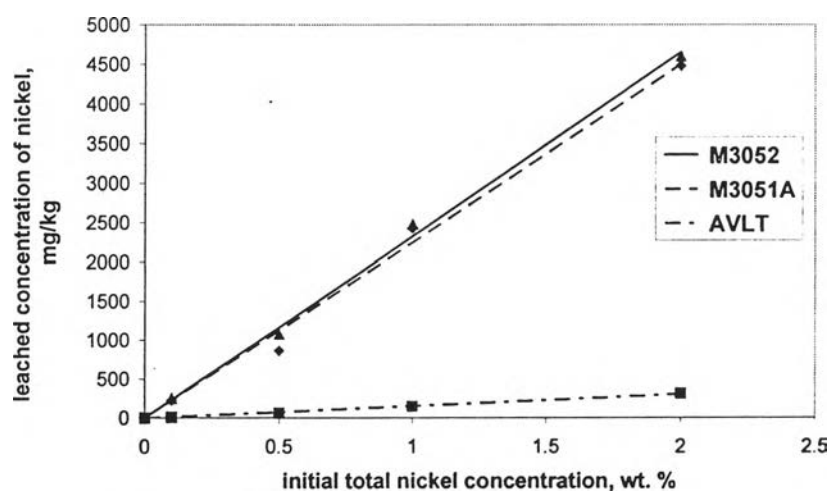


Figure 4.21 Comparison of M3052, M3051A, and AVL

This leaching behavior of nickel might be the effect of a new phases formation of nickel compound in cement. As identify by XRD, Figure 4.23, initial compound (NiO) was found in clinker after burning. Moreover, nickel and Mg was reacted and formed a new phase which was $MgNiO_2$. Other evidence of the new phase forming of $MgNiO_2$ was the clinker morphology analysed by Scanning Electron Microscopy (SEM) as shown in Figure 4.22. More evidences from Stephan et al., 1999, they reported that $MgNiO_2$ was found in the clinker containing with nickel and high concentrations of Mg. Lopez et al., 1998, found a new phase in clinker doped with nickel that had a composition similar to $MgNiO_2$. The previous studied reported that $MgNiO_2$ was a hydrated form which could not have reacted with water (Stephan et al.,

1999). Therefore, these compounds could be the reason for the less leachability of nickel from cement.

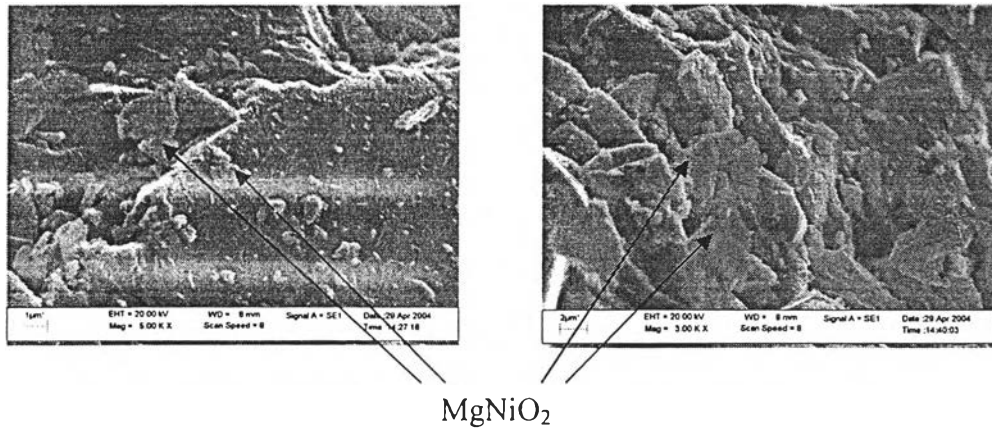


Figure 4.22 Shape of $MgNiO_2$ in obtained clinker

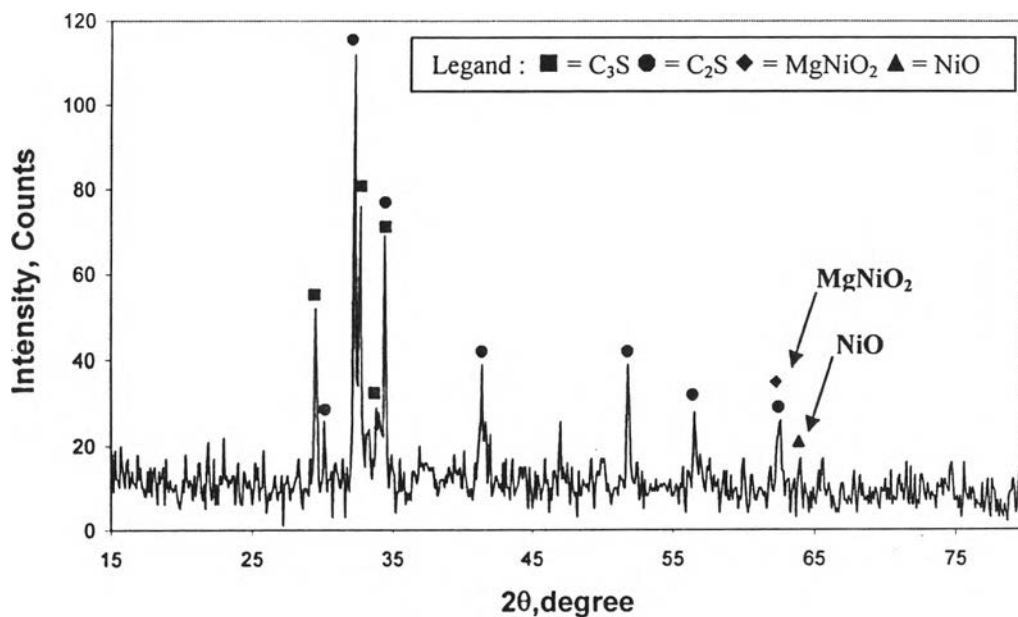


Figure 4.23 XRD pattern of clinker doped with Nickel

Figure 4.24 shows the effects of pH and initial concentrations of nickel on leaching behavior. The results show that in the studied pH range, nickel was effectively leached at pH 4. In comparison between the leached concentrations of nickel and initial concentrations of nickel at pH 4 for each conditions, the leached concentrations of nickel was approximately 0.8-3.28% of initial concentrations of nickel. It was shown that as the cement contaminated with nickel was used and contacted with water at pH 4, maximum nickel could be leached out approximately

3.28% of initial concentrations of nickel. Moreover, as the pH increased, the concentrations of nickel in leachate decreased. At pH range 10-12, there is a few of nickel that can be leached out from cement. This could be explained that nickel is expected to form hydroxide $\text{Ni}(\text{OH})_2$ in the high pH condition. The solubility of nickel hydroxide is minimum at pH 10.2 (Pourbaix, 1994). Most of nickel hydroxide was in a solid form rather than soluble form. Therefore, it might be a reason for low concentration of nickel in leachate for this work.

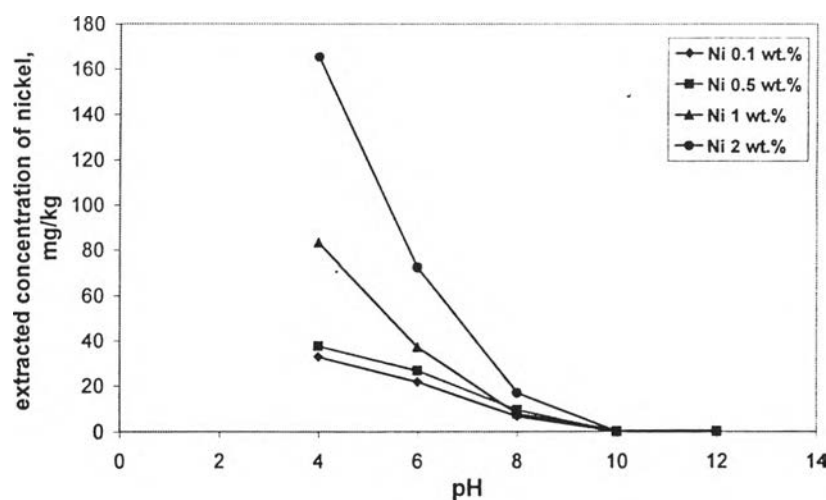


Figure 4.24 Average leached concentrations from pH static leach test

After burning raw material containing nickel, most of nickel were remained in the clinker. When use this clinker for cement production, this cement might be classified as hazardous waste. TCLP and NFMI were applied in order to identify this cement as hazardous waste or non-hazardous waste. According to the Notification of Ministry of Industry No.6 B.E. 2540 and U.S. EPA, the allowable of nickel in the leachate was not regulated. However, in an attempt to quantify the hazard, the U.S. EPA established the guidance that if metal concentrations in the extracts do not exceed the 100 times the maximum concentration levels (MCLs), the waste would not be considered hazardous waste (Cary Hardaway et al., 1999). The MCL of nickel is 0.1 mg/l. Thus, nickel would be considered as hazardous waste, if the concentrations in extracts solution exceeded 10 mg/l. In this research, this criteria was applied to consider the leachate from TCLP and NFMI. As can be seen in Figure 4.25, it shows the results from NFMI. After 18 hours of leaching, the amounts of nickel detected

from 0.1, 0.5, 1, and 2 wt.% of initial concentration of nickel were 0.022, 0.025, 0.026, and 0.031 mg/l, respectively. Moreover, there was no nickel leached from the TCLP test. The leached concentrations from both methods were lower than this criteria. It could be indicated that this cement was likely to be classified as non-hazardous waste. In addition, the lowest concentration of metals which are regulated for TCLP and NFMI was also applied to identify the cement as hazardous waste or non-hazardous waste. The lowest concentration of metals is 0.2 mg/l which is regulated for mercury. In comparison between the lowest concentration of metals and leached concentrations from TCLP and NFMI, the leached concentrations from both test were lower than the regulated concentration. Thus, the cement was likely to be classified as non-hazardous waste. As considering the results from TCLP and NFMI, the results from TCLP were agreed with NFMI. It could be demonstrated that the raw material of cement doped with nickel less than 2 wt.% could not be classified as hazardous waste.

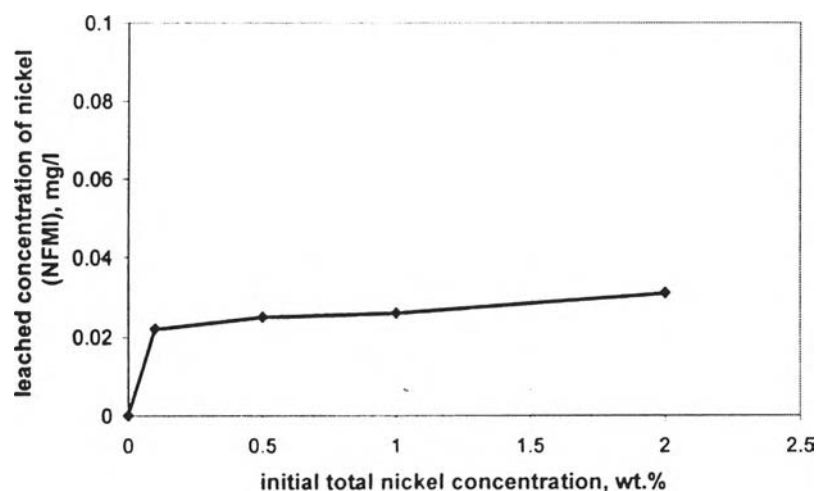


Figure 4.25 Average leached concentration of nickel from NFMI

4.3 Leaching behavior of zinc

Figure 4.26 shows the result obtained from Microwave-assisted leach method 3051A. The results show the total extracted of zinc without zinc in siliceous matrices in cement at different initial concentrations of zinc. It was found that total extracted zinc without zinc in siliceous matrices is a function of initial concentration of zinc. As

initial concentration of zinc increased, the total extracted concentration of zinc increased. The amounts of zinc detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of zinc were 261.67, 1,936.67, 4,216.67, and 9,157 mg/kg, respectively.

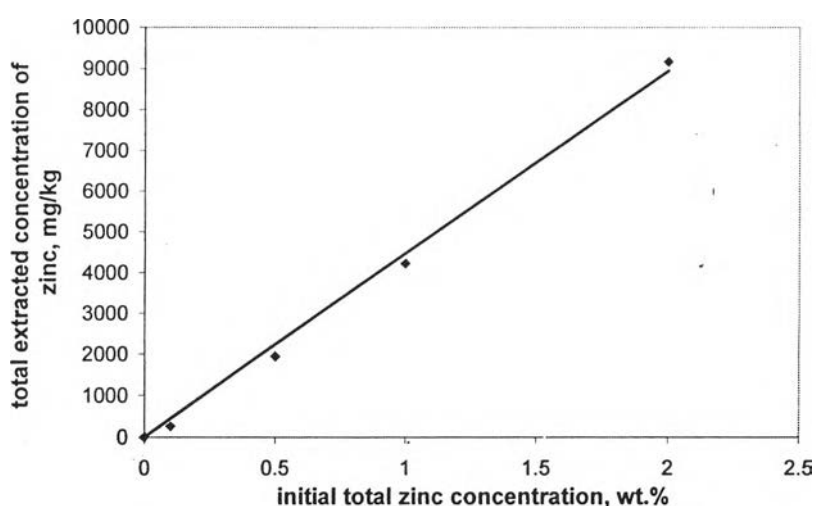


Figure 4.26 Average extracted concentration of zinc from M3051A

Figure 4.27 shows the results obtained from M3052. As can be seen from the result, it was shown that total zinc is a function of initial concentration of zinc. As initial concentration of zinc increased, the total concentration of zinc increased. The amounts of zinc detected from 0.1, 0.5, 1, and 2 wt.% of initial concentrations of zinc were 284.7, 2,083.3, 4,438.3, and 9,670.7 mg/kg, respectively.

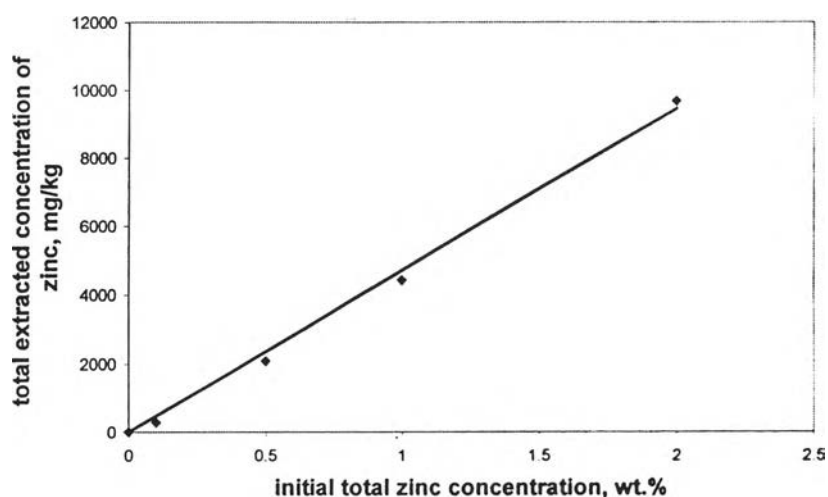


Figure 4.27 Average extracted concentration of zinc from M3052

Figure 4.28 shows the results obtained from availability leaching test (NEN 7341). The results show the maximum concentration of zinc to be leached out from cement at different initial concentration of zinc. From the result, it was found that the maximum concentration of zinc is direct proportional to initial concentration of zinc. The amounts of zinc detected from 0.1, 0.5, 1, and 2 wt.% were 240.66, 1,645.33, 3,627.67, and 8,460.66 mg/kg.

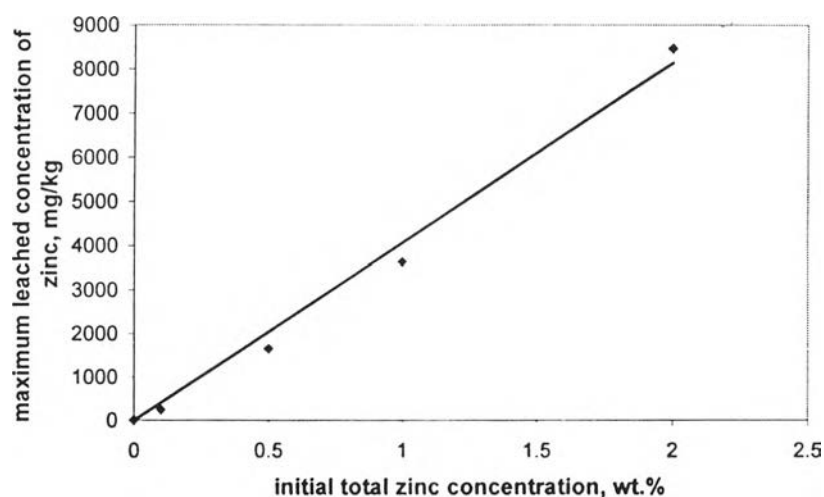


Figure 4.28 Average maximum concentration of zinc from AVL T

Figure 4.29 shows the zinc concentration that leached from obtained cement using different test methods which were AVL T, M3051A and M3052. In comparison the results between M3052 and M3051A, it has been seen that most of zinc in clinker that ready to leach out from cement was not fixed by siliceous matrices of cement. When the results of AVL T were taken to compare with M3051A, it could be indicated that the maximum concentrations of zinc to be leached out at the extreme environmental conditions was approximately 84.95-92.39% of zinc that can be leached from cement. On the basis of AVL T as described earlier, it could be demonstrated that zinc was likely to be leached easily from the cement. However, the leaching of zinc depends mainly on pH of water contacting to the cement. It is needed to explore further details in effect of pH on zinc leaching to obtain amount of zinc that can be leached in each condition. This information was discussed in next section.

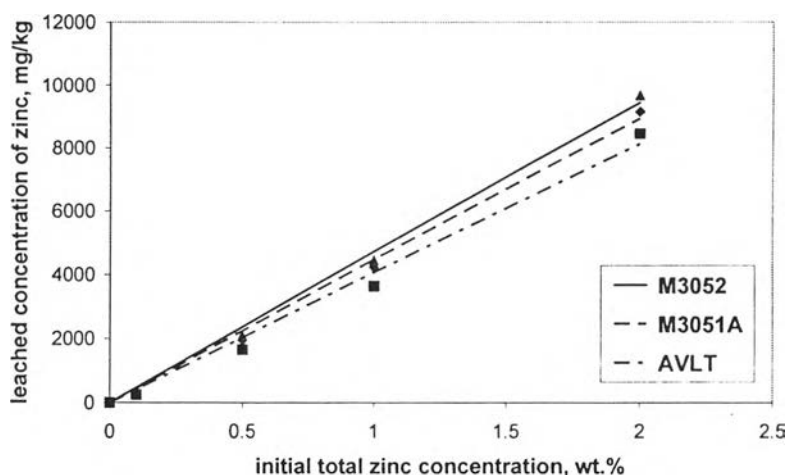


Figure 4.29 Comparison of M3052, M3051A, and AVL T

Figure 4.30 shows the effects of pH and initial concentration of zinc on leaching behavior. The results show that in the studied pH range, zinc was effectively leached at pH 4. As comparing the leached concentrations of zinc with initial concentrations of Zinc at pH 4, it was found that the leached concentrations of zinc was approximately 20.77-23.62% of initial concentrations of zinc. In addition, if the cement contaminated with Zinc was used and contacted with water at pH 4, zinc could be leached out approximately 23.62%. Moreover, as the pH increased, the concentration of zinc in leachate decreased. This leaching behavior might be the reason from a formation of zinc hydroxide in the high pH condition (>8) of cement system (Pourbaix, 1994). In addition, the hydroxy-complexes $Zn(OH)_4^{2-}$ and $Zn(OH)_5^{2-}$ can be present in a strong alkaline solution. They may form the calcium zinc complex hydrate compound $CaZn_2(OH)_6 \cdot H_2O$ (Mollah et al., 1992). This compound can not react with water. Thus, that is a reason for the decreasing of zinc in leachate at high pH condition. Moreover, it was also found that there was no zinc in the leachate at pH 10. Due to the solubility of zinc was minimum at pH 9.3 (Pourbaix, 1994). Most of zinc hydroxide is in a solid form. Therefore, it was not found in the leachate. The obtained results from this research is an agreement with the previous works that the high leachability of zinc was found at pH < 8. (van der Sloot et al., 1996; Li et al., 2001; van der Sloot, 2002)

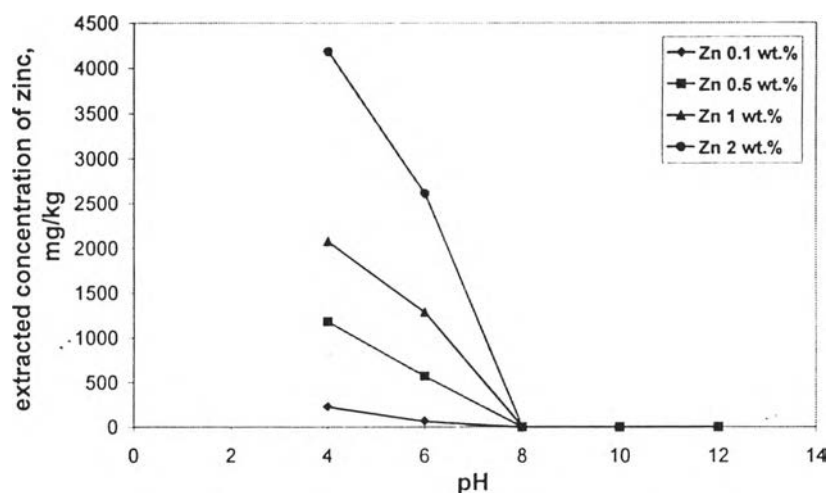


Figure 4.30 Average leached concentration of zinc from pH static leach test

After burning raw material containing zinc, most of zinc were remained in the clinker. When use this clinker for cement production, this cement might be classified as hazardous waste. TCLP and NFMI were applied in order to indentify the cement as hazardous waste or non-hazardous waste. According to the Notification of Ministry of Industry No.6 B.E. 2540 and U.S. EPA, the allowable of zinc in the leachate was not regulated. In an attempt to quantify the hazard, the U.S. EPA established the guidance that if metal concentrations in the extracts do not exceed the 100 times the maximum concentration levels (MCLs), the waste would not be considered hazardous waste (Cary Hardaway et al., 1999). The MCL of zinc is 5 mg/l, which is regulated under a secondary water quality standard. Therefore, zinc would be considered as hazardous waste, if the concentrations in extracts exceeded 500 mg/l. In this research, this criteria was applied to consider the leachate from TCLP and NFMI. The results from TCLP were shown in Figure 4.31. It was found that after 18 hours of leaching (TCLP), there is only 2 wt.% of initial concentration of zinc were detected. The amounts of zinc in the extraction fluid were 0.138 mg/l. The leached concentrations from this method was lower than this criteria. It could be indicated that this cement was likely to be classified as non-hazardous waste. In addition, the lowest concentration of metals which are regulated for TCLP and NFMI was also applied to identify the cement as hazardous waste or non-hazardous waste. The lowest concentration of metals is 0.2 mg/l which is regulated for mercury. In comparison between the lowest concentration of metals and leached concentrations from TCLP,

the leachate from TCLP was lower than the allowable value. Thus, the cement was likely to be classified as non-hazardous waste.

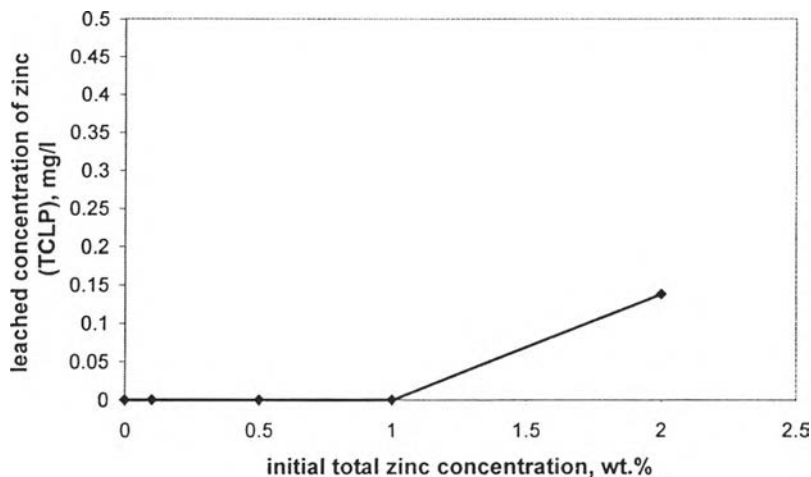


Figure 4.31 Average leached concentration of zinc from TCLP

Figure 4.32 shows the results from NFMI. The results show that after 18 hours of leaching, the amount of zinc detected from 0.1, 0.5, 1, and 2 wt.% were 0.047, 0.221, 0.255, and 0.263 mg/l, respectively. The leached concentrations from this method was lower than this criteria. Thus, this cement was likely to be classified as non-hazardous waste. Moreover, the lowest concentration of metals which are regulated for TCLP and NFMI was also applied to identify the cement as hazardous waste or non-hazardous waste. The lowest concentration of metals is 0.2 mg/l which is regulated for mercury. In considering between the lowest concentration of metals and the leached concentrations of zinc from TCLP and NFMI, the leached concentrations of zinc from both tests mostly exceed the regulated concentration of metals. However, the leached concentrations of zinc were higher than 0.2 mg/l for a little. As considering the hazard between zinc and mercury, it was found that zinc exhibited lower hazard than mercury at the same concentration. Therefore, this cement was likely to be classified as non-hazardous waste. As considering the results from TCLP and NFMI, the results from TCLP were agreed with NFMI. It could be indicated that raw material of cement doped with initial concentration of zinc less than 2 wt.% could be classified as non-hazardous waste.

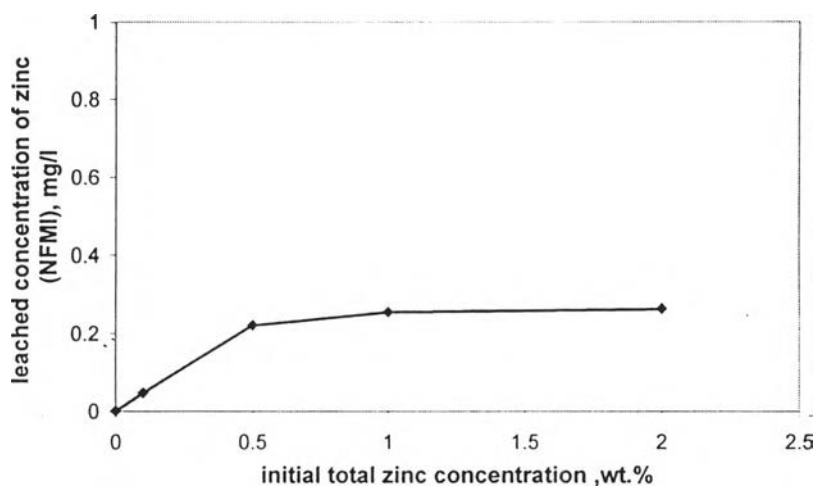


Figure 4.32 Average leached concentration of zinc from NFMI

4.4 Application of this research

The results from this thesis may predict the amount of chromium, nickel, and zinc that can be leached out to environment when they present in the cement raw meal. The results from this thesis exhibit the leaching behavior of chromium, nickel, and zinc from cement when the cement is used and contacted with water on various pH condition. Moreover, the result from toxicity characteristic leaching procedure and Notification of Ministry of Industry No.6 can be the baseline level of chromium, nickel, and zinc in the hazardous waste that are disposed in the cement production process. However, in the real application, the leaching behavior of heavy metals burned with raw meal in rotary kiln should be investigated to ensure that the cement will not be classified as hazardous waste and can use as a cement product.