EXPERIMENTAL STUDY ON OIL WELL CEMENT RESISTANCE TOWARDS HYDROCHCLORIC ACID ATTACK

by

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Dissertation submitted in partial fulfillment of

the requirement for Bachelor of Chemical Engineering (Hons)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

LIM KAH KHENG

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ABSTRACT

Hydrochloric acid (HCl) and Hydrofluoric acid (HF) are used in acidizing treatment to stimulate oil and gas production. It is proven that these acids had successfully increased the oil well production worldwide. However, on the other hand, it has been observed that several oil wells, after submitted to acidizing operations, exhibited zonal intercommunication problems. This is attributed to the occurrence of reactions between the hardened cement slurry in the annulus and the acid. The indication of cement deterioration is the motivation of an extensive experimental program to study the involved mechanisms.

The objectives of this study are to investigate the effect of curing temperature and pressure towards the compressive strength and acid resistance towards Class G oilwell cement. Various concentration of HCl solution is exposed to cement cube samples under different curing condition for the analysis of samples of hardened cement slurries (2-inch cement cube), aiming the verification of changes in chemical compositions due to acid attack. Also, the tests are conducted on the analysis of the acid solutions, aiming the identification and quantification of the elements liberated from the cement into the acid solutions. The techniques of X-ray fluorescence (XRF) , Scanning Electron Microscopy (SEM) and equipment compressive strength tester are to be used for this purpose.

Based on the results, the depth of the acid attack and the influence of the acid solution composition and of the cement chemical composition on the degree of acid attack are to be evaluated. In previous study, it is observed that HCl will react with calcium oxide forming calcium chloride and water. The higher the curing temperature and pressure, the stronger the compressive strength of the sample of cement slurries, leading to the stronger acid attack resistance.

This study will enable a better comprehension of the process of acid attack on cement, and consequently a reduction of this problem in the field will be obtained.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Acidizing treatment is one of the well stimulation method used in oil and gas industry to increase the well production. The treatment is done by pumping treatment fluid near wellbore production region by applying the right pressure either below or above the fracture pressure. [1] Based on the earlier record, acid treatment was performed as earlier as in 1896 and hydrochloric acid (HCl) was the first to stimulate carbonate reservoir. [2]-[4]. Result from this first attempt showed an increase in the well production. Moving from carbonate reservoir to sandstone reservoir, the usage of acid also change to mixture of hydrochloric and hydrofluoric acids. Therefore, since then, many oil companies start to apply this treatment and make some improvement as time pass by.

Past experience shown, although acidizing treatment give positive impact to the well production, the acids used in the treatment also give some side impact that may cause zonal isolation problem. [5]-[9]. Acid attack on cement can occurs on primary or squeeze cementing. Traditional view holds that the acid react with cement in a short period of time until a protective, acid-inhibiting skin formed. However, a significant number of cement squeeze jobs were found to break down or develop isolation problems after HCl/HF acidizing treatment. Field results showed that 75% of squeeze wells broke down when acidized. A failure rate of only 30% was reported for cement squeezed wells that have not been acidized. [10] Also, 17% of the 70 wells that have been stimulated with HCl/HF acid in Eastern Operation Area of Prudhoe Bay Field, Alaska after primary squeezed cement jobs showed zonal isolation problem.[7]

It has been reported that heated and pressurized acid is able to enter micro fractures in the cemented annulus between the casing and formation resulting in significant acid damage to even latex-containing cement.

There are various method been establish to protect the well cement from degrade by acid solutions. Some of the methods are spotting the acid below the cement perforation and using weaker acid such as acetic acid. [10]-[11]. Even with the new technique, the acid can still attack the cement developing zonal isolation problem.

1.2 PROBLEM STATEMENT

Zonal isolation problem has been observed over 70% of the oil wells after submitted to acidizing treatment of hydrochloric acid (HCl), hydrofluoric acid (HF) or combination of these two acids. Acid attack towards the cement results in losing bond between production zones. Another effect of the acid attack is the mass loss of the cement isolating the production zone with formation, leading to potential risk of well collapse as the cement with decreasing mass is no longer able to withstand the formation pressure.

1.3 OBJECTIVE

Upon completing the project, several objectives need to be achieved. The main objectives of this study are as below:

1. To investigate the effect of different curing temperature and pressure of Class G oilwell cement on cement resistance towards HCl attack
2. To quantify the mass loss of Class G oilwell cement before and after HCl acid attack.
3. To quantify the compressive strength of Class G oilwell cement before and after HCl attack.
4. To study the effect of HCl acid attack by the techniques of X-ray Fluorescene (XRF), Scanning Electron Microscopy (SEM).

1.4 SCOPE OF WORK

The scope of works for this study is first identifying the experiment parameters-the curing temperature and pressure and HCl concentration. Upon the setting of experiment parameters, the cement cube will be cured under different variable of curing temperature and pressure. The cement cube then will be exposed to HCl to determine the influence of each curing condition towards the long term sealing integrity of cement. After the acid exposure, the effect of acid attack will be evaluated by the techniques of X-ray Fluorescene (XRF), Scanning Electron Microscopy (SEM) and Compressive Strength Tester.

CHAPTER 2

THEORY & LITERATURE REVIEW

2.1 DEFINITION

I. Compressive strength : Strength is determined by how much weight a material can support or how much stress it can withstand. Compressive strength is the maximum stress that a material will bear when it is subjected to a load that pushes it together.

II. Tensile strength : Tensile strength is the maximum stress a material will bear when it is subjected to a stretching load.

III. Hydrochloric acid, HCI : An acid type commonly used in oil- and gas- well stimulation, especially in carbona'e formations

IV. API Cement : One of several classes of cement manufactured to the specifications of the *American Petroleum Institute (API) Specification 10A*. Classes of API cement are A, B, C, D, E, F, G and H.

V. Cementing : To prepare and pump cement into place in a wellbore. Cementing operations may be undertaken to seal the annulus after a casing string has been run, to seal a lost circulation zone, to set a plug in an existing well from which to push off with directional tools or to plug a well so that it may be abandoned.

2.2 WELL CEMENT CHEMISTRY

Once an oil or gas well is drilled, it is typically lined with steel casing, which is cemented into place. Cement slurry is placed in the annular space to prevent the flow of fluids along the annulus. Abandoned wells are typically sealed with cement plugs inside the casing intended to block the vertical migration of fluids. The permeability and integrity of the cement in the annulus and in the wellbore seal will determine how effective the cement is in preventing fluid leakage.

Wells are typically completed with Portland cement made from raw materials that provide calcium and silica. Calcium is obtained from naturally occurring calcium carbonates such as limestone and coral. The sources of silica include clays and shale. Clays also contain iron oxides (Fe2O3), alumina (Al2O3), and alkalis. These materials are crushed and combined in desired proportions and heated to 1450 °C. The resulting clinker is allowed to cool, mixed with 3-5%gypsum to prevent flash set, and ground to make Portland cement.

2.3 CEMENT HYDRATION

There are four major crystalline compounds in Portland cement: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), and tetracalcium, aluminoferrite ($Ca_4Al_2Fe_2O_{10}$). The most abundant phases in Portland cement are the silicates, comprising over 80 wt % of the cement, mostly in the form of tricalcium silicate. When the compounds of Portland cement are mixed with water, they form hydration products. The main products formed by the cement hydration process are calcium-silicate-hydrate (C-S-H) and calcium hydroxide (Ca(OH)2(s)). C-S-H is a semi-amorphous gel-like material that comprises approximately 70 wt%of the hydrated cement and is the primary binding material. (Note: the C-S-H abbreviation comes from cement chemistry nomenclature, not to be confused with a standard chemical formula.) Ca(OH)2(s) is crystalline and comprises roughly 15-20% of the hydrated cement.

Ca(OH)2(s) deposits nucleate in available capillary pore space during early hydration and grow rapidly to occupy available space between cement grains and early C-S-H deposits.

2. 4 STRENGTH DEVELOPMENT

The conventional way the oil industry has determined strength of cements is by measuring unconfined compressive strength on 2" cubes cured for different periods. This approach is borrowed from the construction industry and is a useful comparative method for different slurry types and designs.

The strength requirement for oil well cements depends on several factors. In general, the cement must have sufficient strength to secure the pipe in the hole, exclude undesirable well fluids, and withstand the shock of drilling, completing and subsequent production loads.In fact, cement needs very little strength to support casing. It is generally accepted that cement tensile or shear strength is around 10% of the compressive strength. A few feet of cement sheath with as little as 50 - 100 psi compressive strength can support several hundred feet of casing. However, filler cements with much higher strengths (1000+ psi) are normally used. It is also common practice to use even higher strength cements (2000+ psi) around the shoe joints and across potential pay zones.

This practice of using high strength cements across the pay zones has been investigated in some detail lately, and available information suggests that very high strength cements, because they tend to be brittle, may not be the best cements to perforate. Lower strength cements, with around 1000 psi compressive strength have been used and perforated across pay zones with good success. Also, foamed cements are used routinely in many wells across the pay zones with excellent results.

Another rule of thumb is that for drilling ahead, the cement needs to develop ~500 psi compressive strength. For offshore applications, however, this practice can be very conservative (long WOC times). For those locations, WOC times have been lowered with good results to the time when the cement has developed ~100 psi. One reason why the industry has looked for high strengths is the effect that even quite low levels of contamination can have on strength. High strength buys extra comfort.

Temperature has a pronounced effect on the strength development. Up to around 230F, increasing temperatures increase strength. However, at higher temperatures than this, decreased strengths are observed with increasing time. This behavior is known as strength retrogression. In order to prevent it, cement formulations exposed to downhole temperatures above 230 deg F are formulated with the addition of about 35% of fine silica. 230 deg F is a rather arbitary cut-off figure. Just below this temperature cement strengths are extremely high and the cement is very brittle. The fact that higher temperatures result in somewhat lower strengths should be seen in context. Above (say) 260 deg F, silica is certainly needed.

2.5 LONG TERM DURABILITY

One very substantial benefit of cement is that it has an established track record of durability – both in the oil industry and the construction industry. The mechanisms of degradation are well understood and, in general, cement once placed and set will remain to provide a pressure seal for a very long time – hundreds of years. There are however some circumstances where this fails. Attack by acid gases and solution – this can cause quite rapid degradation. The best defence is a low permeability – this is obtained through reduced water content and through the use of particles within the slurry, e.g. latex.

Strength retrogression at temperatures higher than 230 deg F is addressed by the addition of silica. Severe cycling of pressures and/or temperatures – this can lead to cracking and eventual movement of fluids. Foamed cements may help to mitigate. Formation movements due perhaps to reservoir compaction or tectonic stresses. The casing may suffer considerable deformation but still remain intact but the cement sheath may crack and allow migration of fluids.

2.6 LITERATURE REVIEW

While there are a number of papers in the literature concerning the attack of acid on cement utilized in civil construction, there has been less work reported on the attack on cement under the conditions applied during the acidization of oilwells.

Fattuhi has studied the deterioration of concrete caused by sulfuric acid. By observing the variation in mass with time of a number of samples, it was verified that the resistance of concrete to attack by sulfuric acid is increased in concrete samples which contain styrene-butadiene latex. **Chandra** studied the resistance of mortars to hydrochloric acid by means of chemical analysis of the samples and **Mehta** evaluated the resistance of concretes to a number of aggressive solutions including hydrochloric, sulfuric, lactic, acetic acids, ammonium sulfate and sodium sulfate based on the loss of mass of the samples upon exposure to these solutions after various times.

Blount specifically treats the problem of resistance of cement utilized in oilwells with respect to attack by hydrochloric and hydrofluoric acids. The author, utilizing the methods proposed by **Brady**, compared the solubilities of different formulations of cement slurries in various acid solutions. Hydrofluoric-based acid react with cement resulting in a significant weight loss. Lab results stimulating field conditions (high pressure / temperature) show that regular cement are soluble up to 96 % in hot HCl-HF acid. Also , acid can extract iron (III) from iron oxides, representing more than 3 % of the cement. The released iron may induce asphaltene precipitation, which stabilize the acid/oil emulsion. The reaction between HCl-HF acid with cement results in formation of Calcium Fluorite (CaF_2), which lead to the formation of protection skin to slow or inhibited the reaction with HCl. Brady investigated the effect of pressure on the solubility of set cement in acids. The study showed that increasing pressure from atmospheric to 1000 psi results in increasing solubility of cement by 25 wt%. According to their analysis, the high pressure would result in high shear rate, which enhance the solubility of cement.

The effect of acids on cement can be minimized by coating the cement by asphalt, synthetic resin or waste pulp liquid (Tahisro and Kubota , 1976). Chemical can be also added to regular cement to reduce acid/cement reactions. These include liquid latex that forms thin coating on the cement particles (Blount et.al, 1991). This film will protect cement from acid attack. Latex that most commonly used includes polyvinyl alcohol (PVA), polyvinyl chloride (PVC) and styrene-butadiene copolymer (Jones and Carpenter, 1991). Fly ash, a silica fume, is another type of additives used to protect cement from acid attack. Fly ash is residue that can be obtained from power plant, which burnt pulverized coal (Davis et.al , 1937). Fly ash reduce the permeability of cement and the amount of highly acid-reactive calcium hydroxide (CaOH) in the cement.

The present work evaluates the resistance of cement cubes to acid based on various approaches. This includes the study of the loss of mass of the samples (utilizing the methods developed by the Research Center of PETROBRAS) and the study of alterations of chemical composition of both the cement cubes and the attacking acid solutions.

CHAPTER 3

METHODOLOGY

3.0 METHODOLOGY OF QUANTIFICATION OF ACID ATTACK ON CEMENT

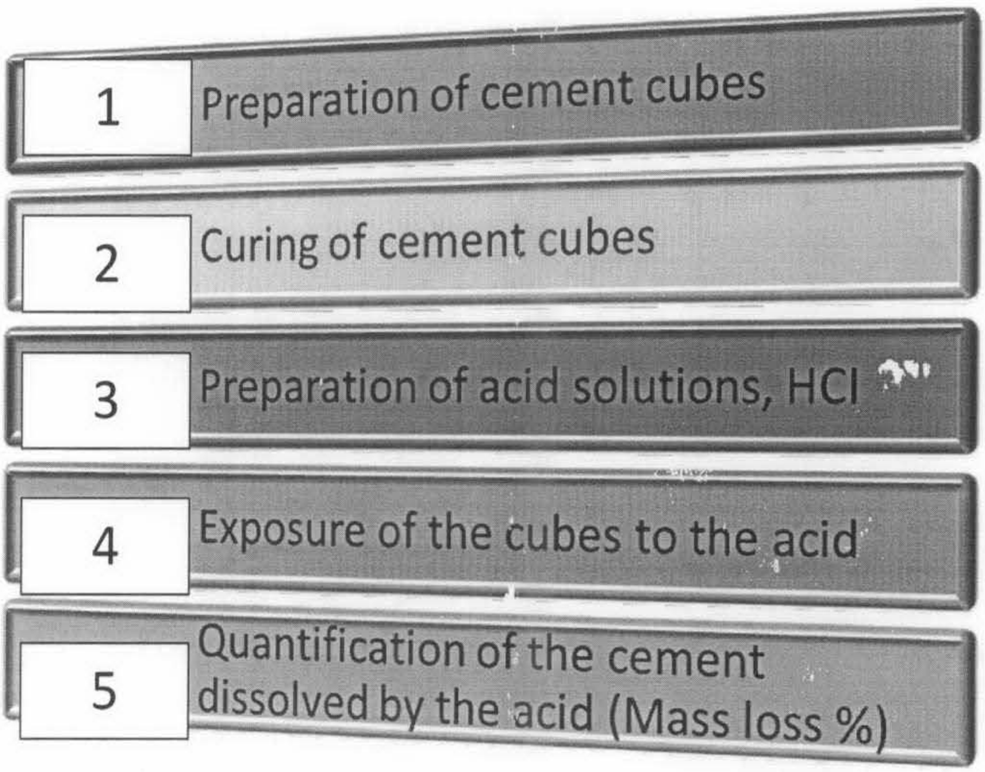


Figure 1 : Methodology of Quantification of Acid Attack on Cement

The method consists essentially of the immersion of cement cubes in a beaker containing acid. One major difference with earlier papers is the immersion time, which is **40 mins** to compare the result with previous paper published. 40 minutes after the start of the test, the cube is removed and its mass loss is determined.

It is worth noting this method has some important differences from the one cited in literature. One of the main differences is the acid volume used – in this case **3 liters** - far greater than the one given in previous paper, that is 250 ml and 750 ml. This prevents false result which can occur if there is no sufficient acid volume to dissolve the cement completely.

3.1 PREPARATION OF CEMENT CUBES

Class G API oil well cement is used for this research paper to standardize the research mechanism with pervious published papers in order to get a comparative result at the end of the research. Based on API standard, Class G oilwell cement is prepared by mixing 792g of Class G cement with 349 g of water. The slurry is then mixed. The preparation of cement cubes is performed by pouring the cement slurry into cubic molds with 5.08 cm sides.

3.2 CURING OF CEMENT CUBES

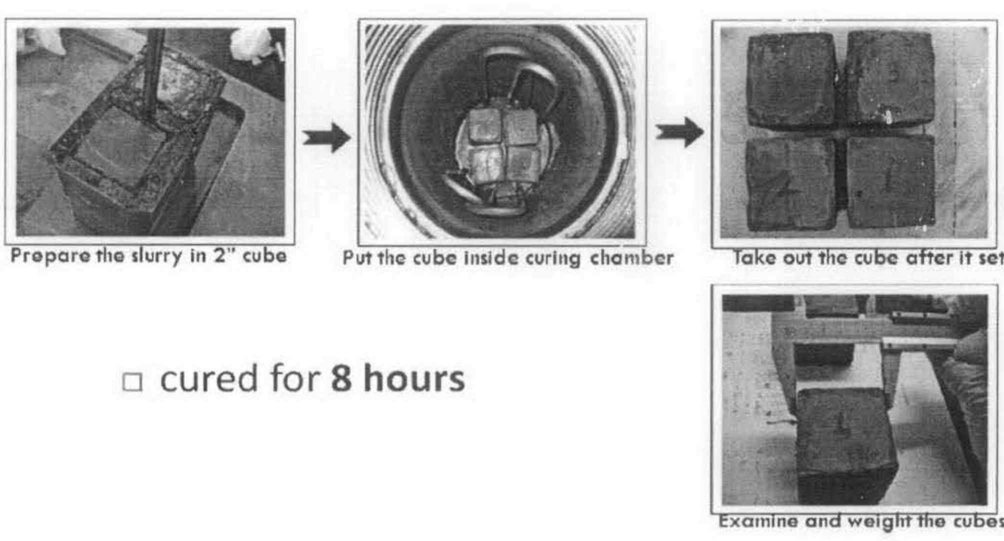


Figure 2 : Curing of Cement Cubes

To determine the effect of curing pressure and temperature towards cement resistance on attack of HCI acid solution, the cement cubes will be cured under the desired conditions as below:

Table 1 : Series of Experiment

Sample Cement Cube	Curing Pressure (psi)	Curing Temperature (^{O}F)
1	3000	175
2	4000	175
3	5000	175
4	3000	90
5	3000	150
6	3000	200

The cubes are often cured for **8 hours** under desired conditions of temperature and pressure. Following the cure, the sample are demolded and washed to remove the grease form their surfaces. The cubes are then examined and only the most perfect cubes are accepted for testing to avoid any interference on the result due to surface imperfection of cubes. Prior to acid immersion, the cubes are weighted and initial mass recorded.

3.3 PREPARATION OF HCI ACID SOLUTION

Towards the end of curing process, HCl acid solution in desired concentrations will be prepared as below:

Table 2 : Preparation of HCI Acid solution

HCI acid solution	Concentration (%)
1	12

980 ml of distilled water are mixed with 2020 ml of 37% of concentrated HCl to produce 3L of 12 % HCl acid solution.

3.4 EXPOSURE OF CEMENT CUBES INTO HCI ACID SOLUTION

A beaker containing 3 liters of the acid is placed in a thermostatically controlled water bath. A second beaker with the same volume of water is placed alongside it as temperature control, because the hydrochloric acid would attack the glass of the thermometer if it is put directly in acid solution. The test were conducted at 65 °C. As soon as the acid reaches this temperature, the cement cube is placed in beaker of acid. The test is performed without any agitation of acid, as the solubility of cement cubes in the similar acid solution was not increased by agitation at 200 rpm, in comparison to the acid which is not agitated. Immersion of 2" cement cubes in HCI acid solution is 40 minutes as proposed in paper published.

3.5 QUANTIFICATION OF CEMENT CUBES DISSOLVED BY THE ACID

40 minutes after the start of the test, the cube is removed from the solution and allowed to dry at room temperature for 1 hour. The cube is then weighted and final mass recorded. The quantification of consumption of cement by the acid is expressed in term of loss of mass, according to the following equation:

Mass Loss (%) = [(Initial mass- final mass)]/ initial mass x 100

3.6 POST ANALYSIS OF ACID ATTACK

Attack of HCl acid solutions on 2" cement cubes will be analyzed from the following perspective:

1. Compressive Strength
2. Mass loss % analysis
3. X-ray Florescence (XRF)
4. Scanning Electron Microscopy (SEM)

3.7 ANALYSIS OF THE HARDENED CEMENT CUBES

The samples of cement cubes both attacked and unattacked by cement were analyzed by means of **x-ray fluorescence (XRF)** in order to verify the alternation in the chemical composition caused by the acid attack. To evaluate the acid attack and verify the depth to which alternation occur owing to the acid, the samples were cut into 3 mm layers by means of diamond saw for XRF studies .

XRF was also performed for elemental analysis of the sample before and after attack of the acids. With these methods, it is possible to observe and compare alternation caused by acid as well as the depth of penetration of the alternations. In addition, quantitative and semi-quantitative XRF studies were performed. Those analyses of sample surface were semi-quantitative due to small amount available at distinctive, white surface layer. The inner layers were analyzed quantitatively by XRF.

The samples were also observed by **Scanning Electron Microscopy (SEM)**. SEM can produce high resolution images on sample surface, which permits the micro-elemental analysis on the surface.

3.8 ANALYSIS OF CEMENT STRENGTH

API RP-10B includes two methods to measure the strength development of cements. One is the destructive test referred to above using 2 inch cubes cured in moulds at simulated downhole conditions. The other uses a special device known as the Ultrasonic Cement Analyzer (UCA). **In this research, Destructive test will be applied to cement cubes.**

CHAPTER 4

RESULT AND DISCUSSION

In this chapter, the results of this study are discussed. Each of the samples show different degree of hydrochloric acid attack due to the difference in curing pressure and temperature. Although the pure slurry is not utilized in casing cement operation, this study serves to perfect the method of analysis and as a baseline to compare with other formulation.

Previous study by Miranda et.al found that the main components of the cement cubes are SiO_2 and CaO with the average percentage of 20% and 60% respectively.

Theoretically, HCl will react with CaO producing calcium chloride and water while HF will react with SiO_2 producing silicon tetrafluoride and water. Silicon tetrafluride then react with fluoride ion to produce silicon hexafluoride as the end product. The reaction mechanisms are as below.

$$\mathbf{2HCl + CaO \rightarrow CaCl_2 + H_2O} \quad \textbf{(1)}$$ **Main reaction for this research paper**

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \quad (2)$$

$$SiF_4 + 2F^- \rightarrow SiF_6^{2-} \quad (3)$$

In this study, the attack of HCl towards CaO (Equation 1) is focused.

Cement cube degradation by acid attack is caused by the reaction of the acid with the cement hydration products forming soluble salts, mostly with calcium. The weight loss is caused by leaching of these soluble products. Also, the formation of the double salts produces expansion and gives rise to disintegrating stresses in the cement cube, which fall apart. The acid attack starts on surface, diffusing to a greater extend by reacting with the cementitious matrix.

The degree of leaching by calcium dissolution is proportional to the square root of time (non-steady state diffusion) since the diffusion kinetics slows down with time. After a transitory time, the conditions for local chemical equilibrium are achieved inside the cement cube. Due to high solubility on the surface layer, the cement cube will have high surface dissolution rate, and after a short time, the kinetics of degradation will follow the $t^{1/2}$ law.

When the curing temperature and pressure increases, the compressive strength of cement cube is raised. It is observed that the distribution of CaO and SiO_2 crystal of higher curing temperature and pressure are more even distributed compared to lower curing condition. In other words, it indicates that the solubility of CaO and SiO_2 will decrease with increase temperature and pressure, leading to the lower amount of mass loss over the attack of HCl solution.

The impact of air bubbles present in slurries is significant. It directly reduces the compressive strength of cement cube samples. Thus, air bubbles in the slurries must be "knocked out" by spatula during cement slurries preparation stage before going into curing phase to eliminate the "air bubble factor" towards end result.

The concentration of HCl solution plays the vital role in determining the mass loss (cement consumption) of cement cube. With higher concentration of acid solution, it is observed that more free ions H^+ could be released for reaction. In another word, with higher concentration of acid solution, the reaction between HCl and CaO become more vigorously.

4.1 MASS LOSS %

Table 3 : Mass Loss % - Pure Class G Cement Slurry and 12 % HCl

		Mass (g)		Dimension (mm)			Average	Mass	Average
	SAMPLE	Before	After	Before	After	Mass Loss (%)	Mass Loss (%)	Loss (g)	Mass Loss (g)
3000 psi 90 °F	Cube 1	250.80	213.85	50.85 x 49.38	50.44 x 48.92	14.73285486	14.13	36.95	35.45
	Cube 2	250.80	216.85	50.85 x 49.38	50.44 x 48.92	13.53668262		33.95	
	Cylinder 1	112.05	95.96	38.40 (D) 50.30 (H)	37.50 (D) 48.70 (H)	14.35966087	14.43	16.09	16.21
	Cylinder 2	112.68	96.34	38.20 (D) 50.75 (H)	37.40 (D) 50.40 (H)	14.50124246		16.34	
		Mass (g)		**Dimension (mm)**			**Average**	**Mass**	**Average**
	SAMPLE	**Before**	**After**	**Before**	**After**	**Mass Loss (%)**	**Mass Loss (%)**	**Loss (g)**	**Mass Loss (g)**
3000 psi 150 °F	Cube 1	251.60	224.53	50.80 x 51.00	50.60 x 50.90	10.75914149	11.33	27.07	28.62
	Cube 2	253.34	223.17	50.80 x 50.90	50.75 x 50.54	11.90889713		30.17	
	Cylinder 1	109.54	96.00	38.40 (D) 50.30 (H)	37.60 (D) 50.00 (H)	12.36078145	11.92	13.54	13.26
	Cylinder 2	113.04	100.06	38.20 (D) 50.75 (H)	37.53 (D) 50.30 (H)	11.48266100		12.98	

		Mass (g)		Dimension (mm)			Average	Mass	Average
	SAMPLE	Before	After	Before	After	Mass Loss (%)	Mass Loss (%)	Loss (g)	Mass Loss (g)
3000 psi 200 °F	Cube 1	247.43	223.80	50.80 x 50.80	50.00 x 50.22	9.550175807	9.89	23.63	24.58
	Cube 2	249.60	224.06	50.90 x 51.30	50.45 x 50.65	10.23237179		25.54	
	Cylinder 1	109.38	100.30	38.00 (D) 49.60 (H)	37.58(D) 49.22 (H)	8.301334796	8.24	9.08	9.15
	Cylinder 2	112.73	103.50	38.00 (D) 50.80 (H)	37.56(D) 50.63 (H)	8.187705136		9.23	

		Mass (g)		Dimension (mm)			Average	Mass	Average
	SAMPLE	Before	After	Before	After	Mass Loss (%)	Mass Loss (%)	Loss (g)	Mass Loss (g)
3000 psi 175 °F	Cube 1	250.10	222.26	50.92 x 50.94	50.35 x 50.40	11.13154738	10.40	27.84	26.00
	Cube 2	249.60	225.44	50.92 x 50.00	50.41 x 50.37	9.679487179		24.16	
	Cylinder 1	113.00	102.50	38.26 (D) 50.96 (H)	37.50 (D) 50.54 (H)	9.292035398	9.23	10.50	10.45
	Cylinder 2	113.45	103.04	39.18 (D) 50.98 (H)	38.00 (D) 50.30 (H)	9.175848391		10.41	

	SAMPLE	Mass (g) Before	After	Dimension (mm) Before	After	Mass Loss (%)	Average Mass Loss (%)	Mass Loss (g)	Average Mass Loss (g)
4000 psi 175 °F	Cube 1	249.80	228.20	50.92 x 50.94	50.41 x 50.40	8.646917534	9.08	21.60	22.70
	Cube 2	250.20	226.40	50.92 x 50.00	50.43 x 50.40	9.512390088		23.80	
	Cylinder 1	112.52	103.00	37.98 (D) 50.80 (H)	37.46 (D) 50.49 (H)	8.460718095	8.43	9.52	9.52
	Cylinder 2	113.32	103.80	37.96 (D) 51.40 (H)	37.46 (D)51.14 (H)	8.400988352		9.52	
	SAMPLE	Mass (g) Before	After	Dimension (mm) Before	After	Mass Loss (%)	Average Mass Loss (%)	Mass Loss (g)	Average Mass Loss (g)
5000 psi 175 °F	Cube 1	249.3	227.4	50.85 x 50.92	50.51 x 50.40	8.784596871	8.39	21.90	20.90
	Cube 2	249.3	229.4	50.85 x 50.92	50.51 x 50.40	7.982350582		19.90	
	Cylinder 1	102.8	94.6	37.96 (D) 47.36 (H)	37.37 (D) 46.20 (H)	7.976653696	7.98	8.20	8.20
	Cylinder 2	102.8	94.6	37.96 (D) 47.36 (H)	37.37 (D) 46.20 (H)	7.976653696		8.20	

Table 4 : Effect of Curing Temperature on Cement resistance towards HCl attack

Temperature (Degree F)	Mass loss %
90	14.13
150	11.33
175	10.4
200	9.89

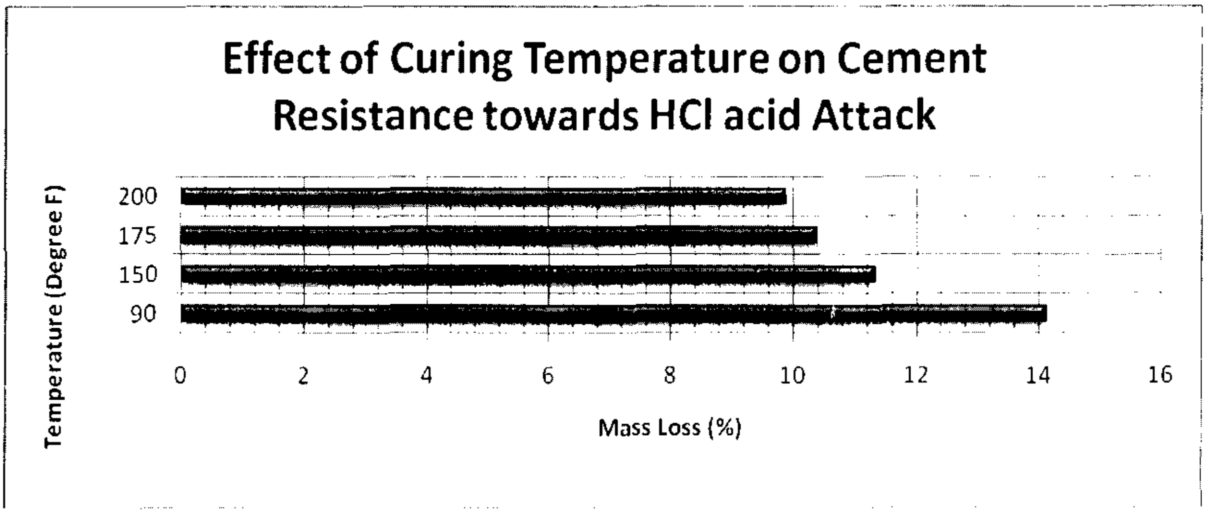


Figure 3 : Effect of Curing Temperature on Cement resistance towards HCl attack

The first series of test is meant to determine the effect of temperature on the cement strength development during the first 8 hours of curing. With the curing pressure fixed at 3000psi, the curing temperature is increased gradually from 90 degree F to 200 degree F. Mass loss % has been used as the measure to quantify HCl acid solution attack towards Class G cement. The results of mass loss % in Figure 3 has shown us that **the increase of temperature raise the strength of cement during the first 8 hours of strength development**. The range of mass loss % is from 9 to 15 %. Cement cube with curing condition of 3000 psi and 90 degree F is found suffered the most severe mass loss%, which is 14.13 %. The high definition image of acid attack on this cube will be shown under Scanning Electron Microscopy (SEM) section.

From the research, It is found that the increase of temperature reduces the cement permeability. As a result, the acid solubility of CaO will be significantly reduced, leading to lesser mass loss %. Temperature has pronounced positive effect on cement resistance towards HCL acid attack. In some of the cement development literature, it is found that up to around 230F, increasing temperatures increase strength. However, at higher temperatures than this, decreased strengths are observed with increasing time. This behavior is called strength retrogression. Therefore. In order to further enhance this research work, it is recommended that temperature over 230 degree F to be included in the next phase of research.

Table 5 : Effect of Curing Pressure on Cement resistance towards HCl attack

Pressure (psi)	Mass loss %
3000	10.4
4000	9.07
5000	8.38

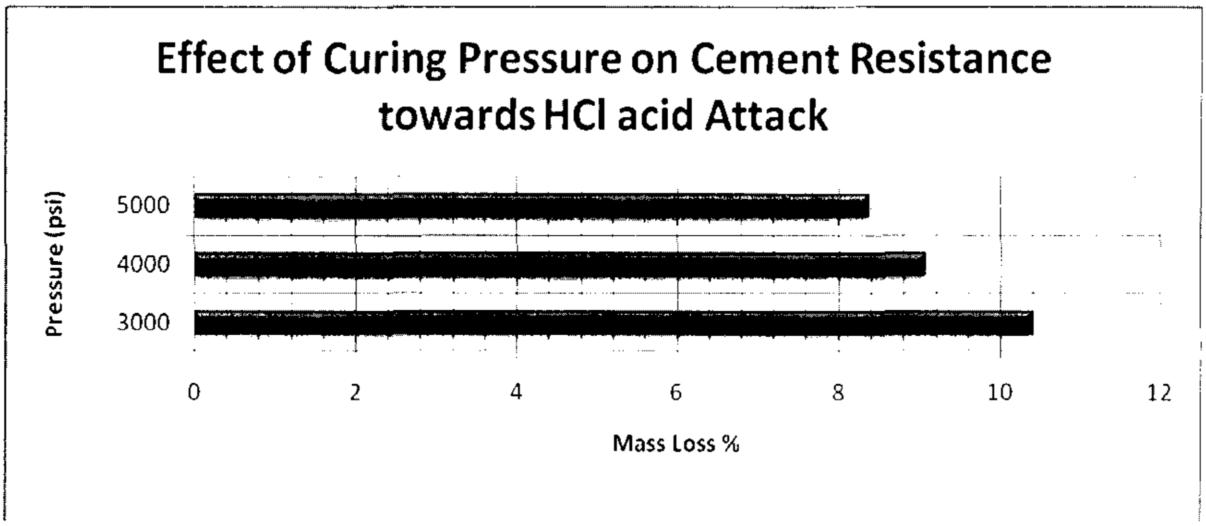


Figure 4 : Effect of Curing Pressure on Cement resistance towards HCl attack

The second series of test is to determine the effect of curing Pressure on the cement strength development during the first 8 hours of curing. With the temperature of 175 degree F fixed, the Pressure of 3000 psi, 4000 psi and 5000 psi is set. The selection of the following Pressure range is based on the lower and upper limit of Malaysia oilfields pressure condition which range from 3000 psi to 5000 psi. From the Figure 4 ,mass loss % results shown that the increase of pressure from 3000 psi to 5000 psi has increasing positive impact on the cement resistance towards HCL acid attack. Several authors have shown that curing pressure above 2000psi can be negligible on the development of 24 hour compressive strength on neat cement with curing temperature of 2000 psi. However, development of 8-hour compressive strength has shown to have increasing trend with increasing curing pressure. Therefore, as a conclusion, the impact of curing temperature is far greater than curing pressure on Class G cement resistance towards HCl attack.

4.2 COMPRESSIVE STRENGTH TESTING

Table 6 : Compressive Strength Testing of cement cube

			Average Max. Load (N/ m2)		Compressive strength Reduction (N/m2)
no.	**Curing Pressure (psi)**	**Curing Temperature (degree F)**	**BEFORE**	**AFTER**	
1	3000	90	113900	72400	41500
2	3000	150	115300	84850	30450
3	3000	175	117300	103600	13700
4	3000	200	120000	107900	12100
5	4000	175	119100	108800	10300
6	5000	175	119900	109800	10100

As expected from the result of mass loss % , the cement cube cured under condition of 5000 psi and 175 degree F has lowest compressive strength reduction while the cement cube cured under 3000 psi and 90 degree F has the highest compressive strength reduction. Again from the result of the compressive strength testing, it proves that higher curing temperature and pressure contribute to the stronger strength development of cement cube during the first 8 hours of curing.

4.3 X-RAY FLUORESCENCE (XRF)

The purpose of XRF is determine the chemical elements both qualitatively and quantitatively by measuring their radiation characteristic. In this research, Bruker S-4 Pioneer XRF Machine is used. The most abundant phases in Portland cement are the silicates, comprising over 80 wt % of the cement, mostly in the form of tricalcium silicate (Ca_3SiO_5). White powder is observed at the surface of each cement cube after HCl attack. The table below summarizes the percentage (%) of each element exist in the cement.

Table 7 : XRF elemental analysis of cement cube before and after HCl attack

Element	Percentage (%)							
	Before Attack	After Attack						
	SURFACE	MIDDLE	SURFACE					
	3000 psi	3000 psi	3000 psi	3000 psi	3000 psi	3000 psi	4000 psi	5000 psi
	175°F	175°F	90 °F	150 °F	175 °F	200 °F	175 °F	175 °F
SiO_2	23.100	22.900	23.200	22.800	23.060	21.680	22.930	23.120
MgO	0.790	0.743	0.750	0.723	0.732	0.786	0.772	0.773
P_2O_5	1.170	1.170	1.140	1.180	1.150	1.190	1.118	1.150
SO_3	1.430	1.420	1.410	1.440	1.420	1.410	1.420	1.450
Al_2O_3	2.380	2.300	2.400	2.310	2.220	2.190	2.230	2.350

TiO_2	0.140	0.138	0.135	0.135	0.141	0.145	0.139	0.142
Fe_2O_3	4.561	4.582	4.559	4.518	4.418	4.491	4.512	4.563
ZnO	0.126	0.115	0.123	0.128	0.119	0.113	0.124	0.113
CuO	0.103	0.104	0.103	0.103	0.103	0.103	0.103	0.103
CaO	66.200	65.800	59.570	60.963	62.071	63.596	62.346	62.573
$CaCl_2$	0	0	5.610	4.700	4.566	4.296	4.244	3.663

In all the samples composed by pure cement slurries and attacked by 12 % HCl solution, white solid precipitate was found on surface. By XRF, the white solid precipitate is identified as **Calcium Chlorine ($CaCl_2$)** which was expected from the reaction between Calcium Oxide and Chlorine ion in HCl. The cement cube cured under 3000 psi, 90 °F is found contains the most amount of $CaCl_2$, indicating that reaction occurs most vigorously with this curing condition. The observation matches the finding from mass loss %, in which under this curing condition, the cement cube suffers the most severe mass loss.

Compared to un-attacked cement surface, all the samples exposed to HCl exhibit the lower amount of CaO in percentage with cement cube cured under 3000 psi, 90 °F has the greatest loss of CaO.

For all the cement cubes exposed to HCl solution, the amount of SiO_2 is equivalent to the reference cube (un-attacked cement cube). It signifies that SiO_2 does not take place in the reaction.

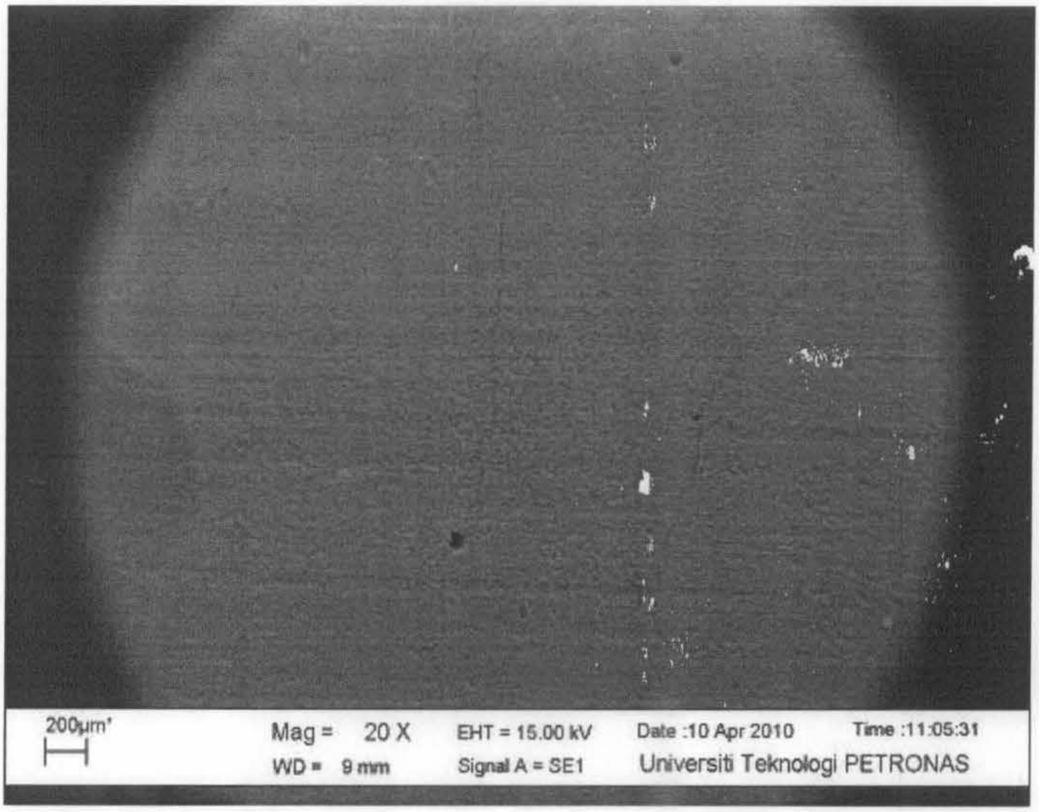
Beyond the 1st cut layer (3mm from surface), the concentration is equivalent to the reference cube. Therefore, XRF confirmed the observation that the alteration only occurs on surface.

4.4 SCANNING ELECTRON MICROSCOPY (SEM)

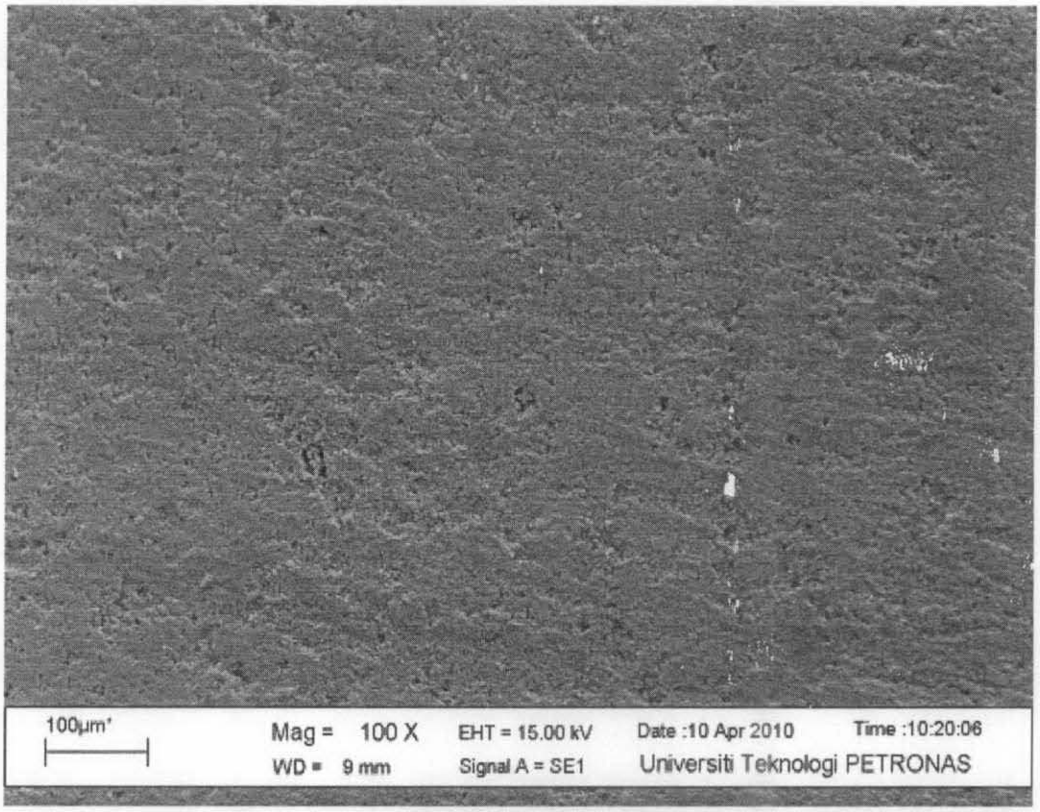
A core chip with a freshly broken surface is coated with a gold palladium alloy and placed in the vacuum chamber of the SEM. The core chip is viewed at high magnification and a photomicrograph is taken. The SEM machine used in this research is VP1430 Brand Leo. The photomicrographs are shown below with 3 magnification - 20x, 100 x and 500x.

4.4.1 Initial test (Reference cube)

SURFACE - 3000 psi, 175 ^{O}F



The cement cube is "clean" and free of any sign of attack. The little tiny crack on cement cube surface might be the cause of defect during the cement preparation stage when cement cube is taken out from curing chamber equipment. The chemical alteration of cement cube before HCl attack is neat and well-distributed.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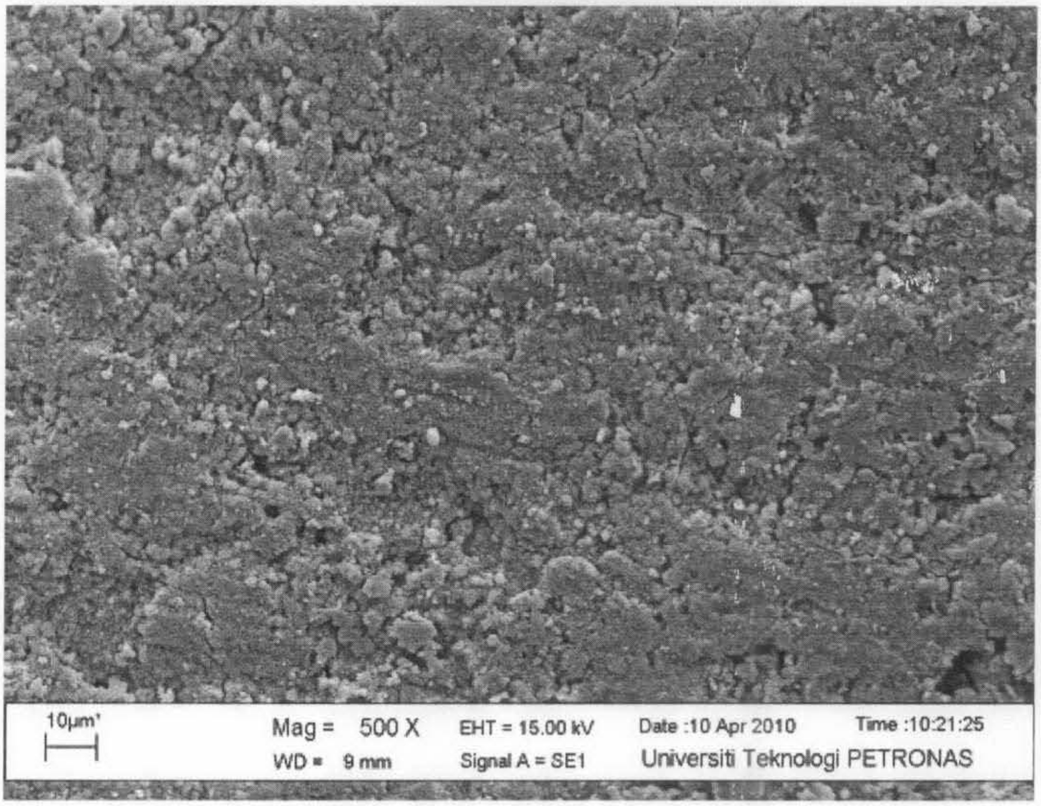
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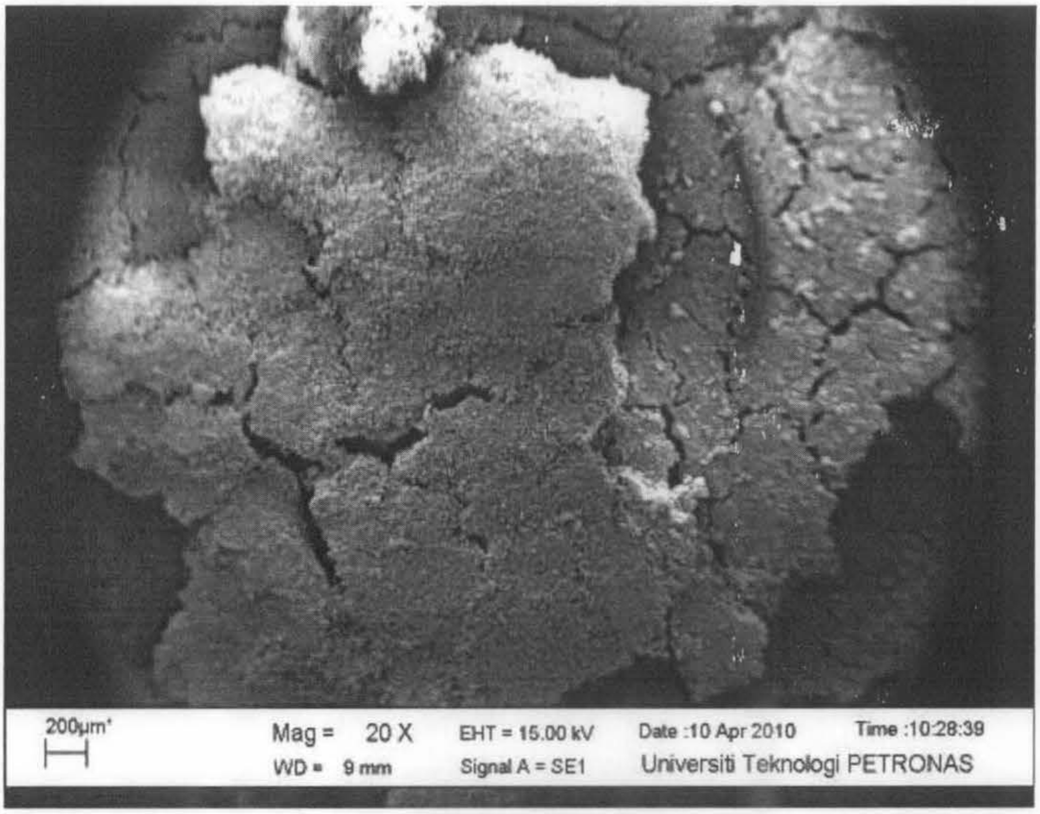
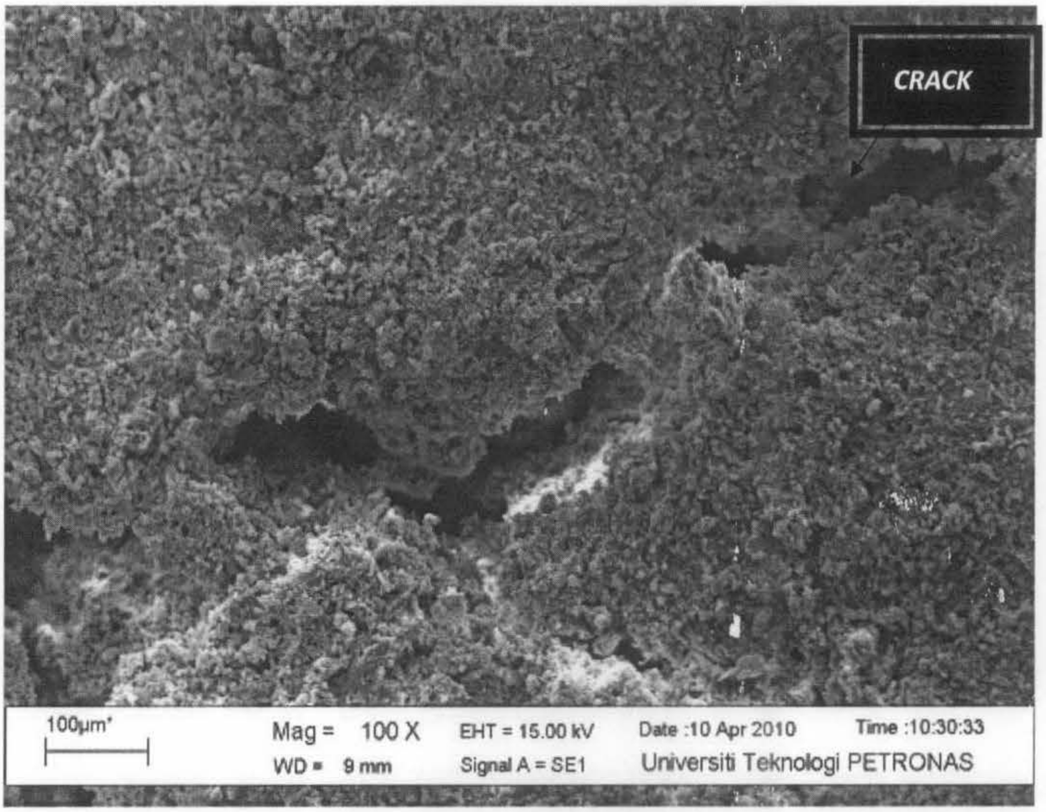
4.4.2 Post HCl Attack

SURFACE - 3000 psi, 90 °F



At the this curing condition, the cement cube suffered the most severe attack and crack, which is 14.13 mass loss %. Even with the magnification of 20x, the crack is so obvious to be observed by naked eye. White powder precipitate is found on cement cube surface after the contact with HCl. The crack is deep and surface chemcial alteration is disturbed by HCl attack. If sigifies that the lower curing temperature contributes to the greater HCl attack on cube surface. The weight loss is caused by leaching of these soluble products. Also, the formation of the double salts produces expansion and gives rise to disintegrating stresses in the cement cube, which fall apart. The acid attack starts on surface, diffusing to a greater extend by reacting with the cementitious matrix.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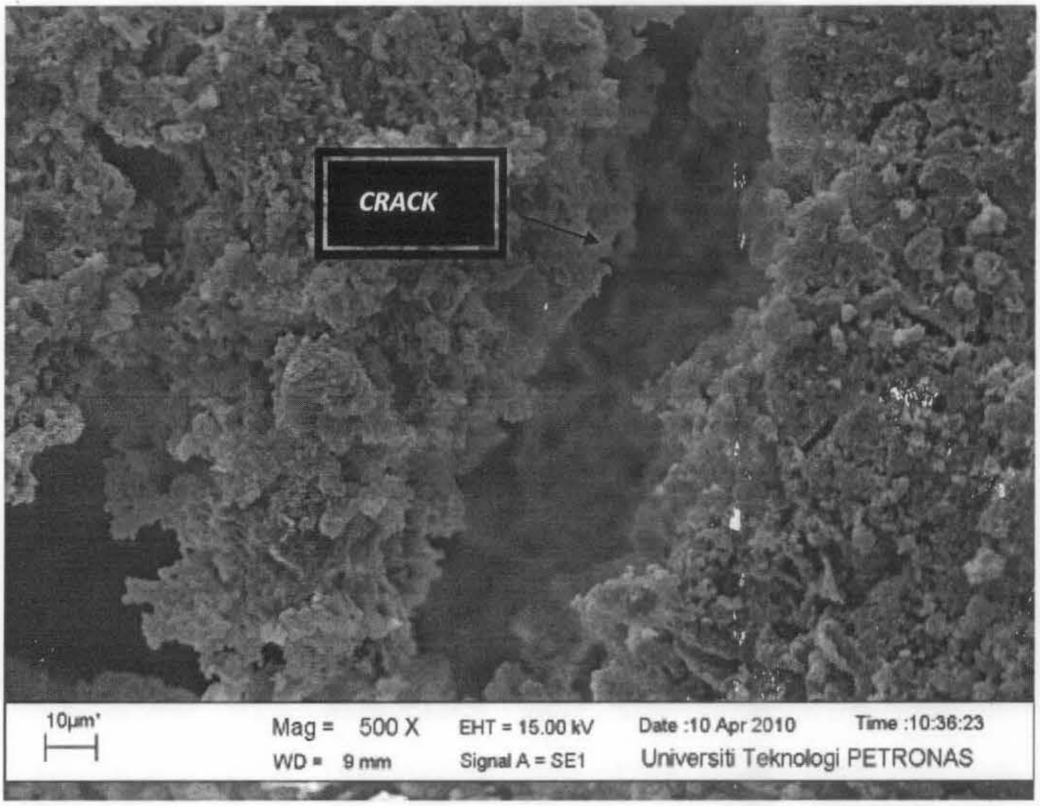
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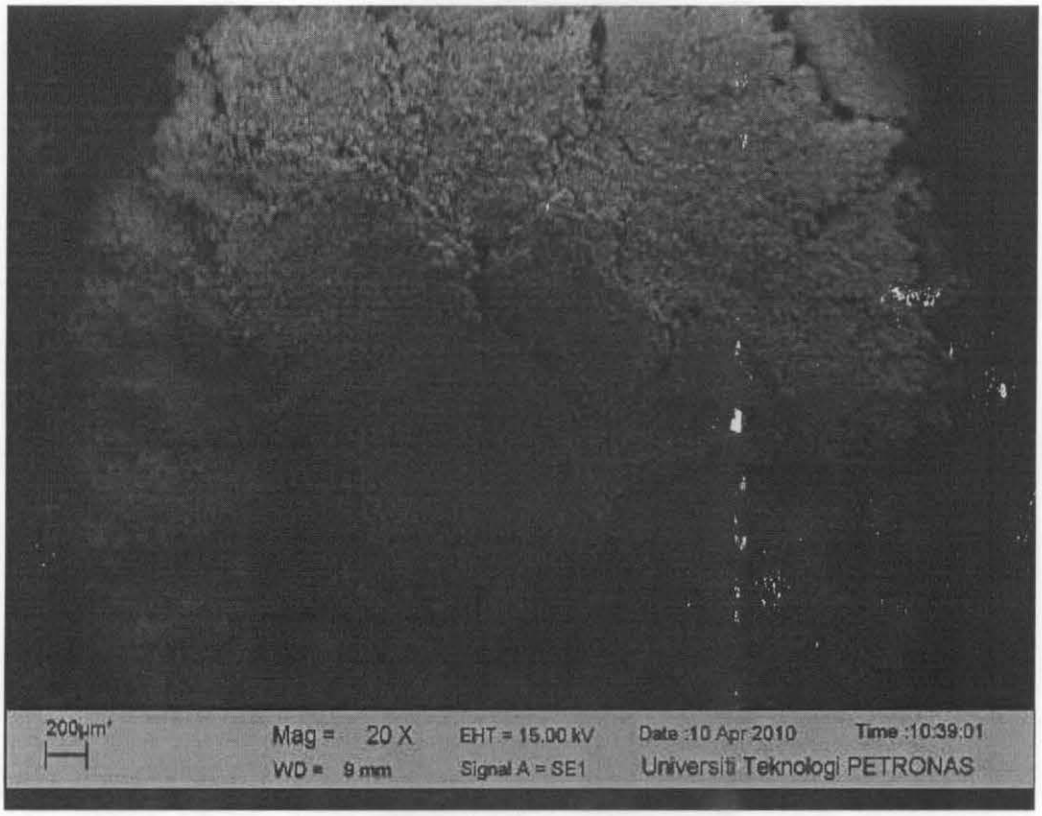
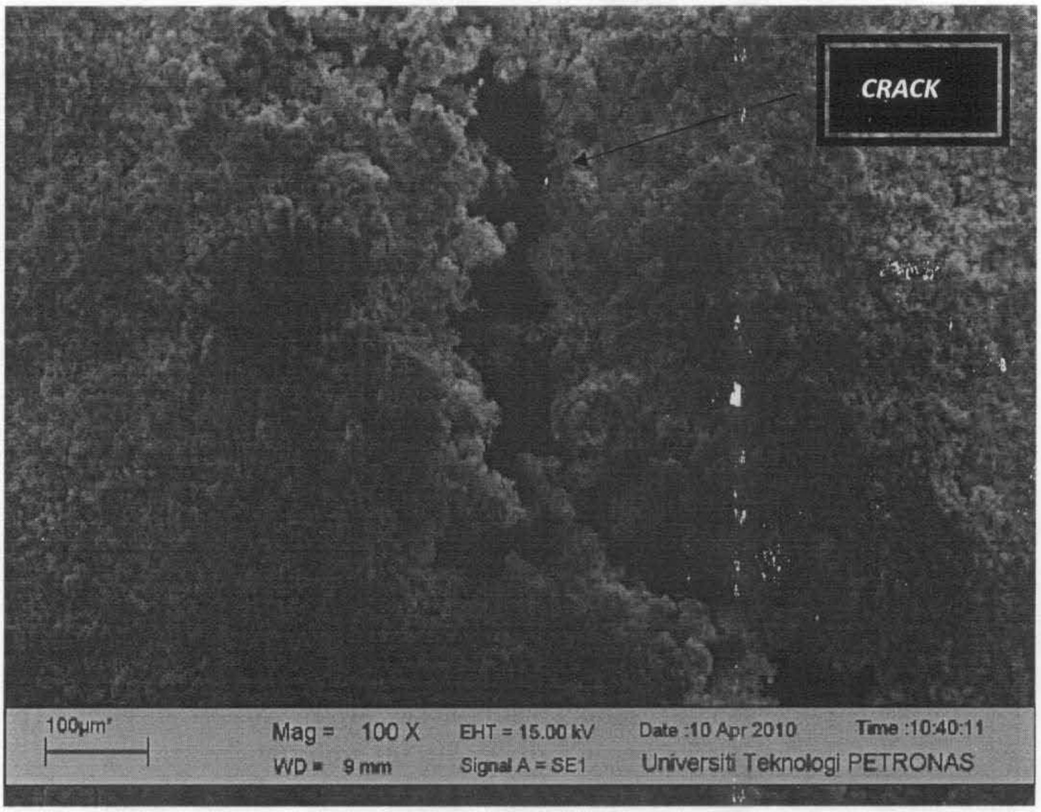
SURFACE - 3000 psi, 150 °F



Under this curing condition, the cement cube suffers the mass loss of 11.33 %, which is lower than one cured under the temperature of 90 ^{O}F. White powder precipitate is found on cement cube surface after the contact with HCl. Crack ecixts on the cube surface. The chemical alteration has been disrurbed by the HCl attack.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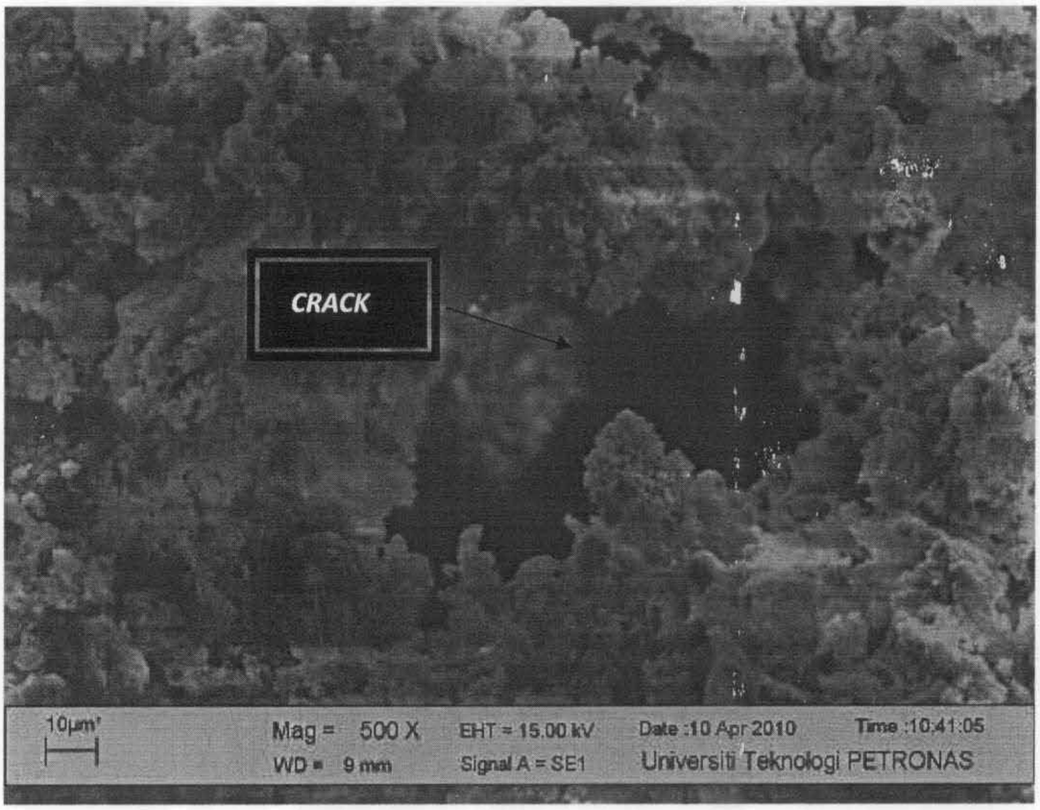
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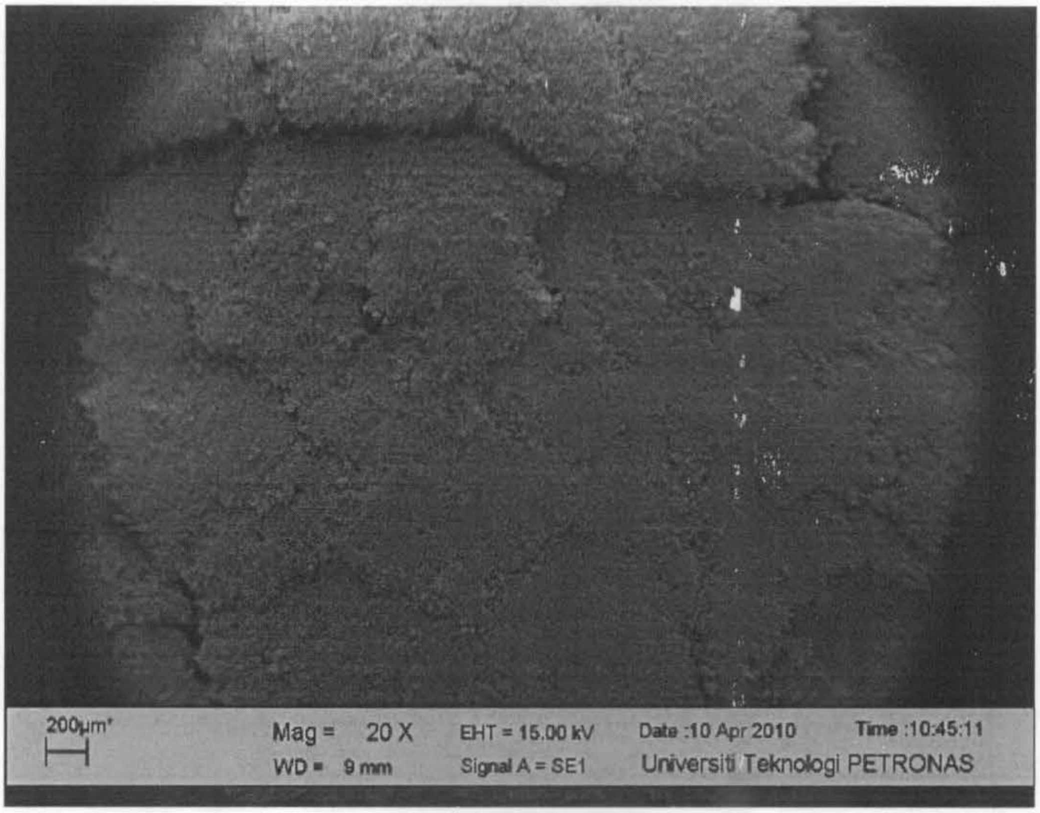
SURFACE - 3000 psi, 175 °F



Under this curing condition, the cement cube suffers the mass loss of 10.40 %, which is lower than one cured under the temperature of 90 ^{O}F and 150 ^{O}F. White powder precipitate is found on cement cube surface after the contact with HCl. Crack ecixts on the cube surface. The chemical alteration has been disrurbed by the HCl attack.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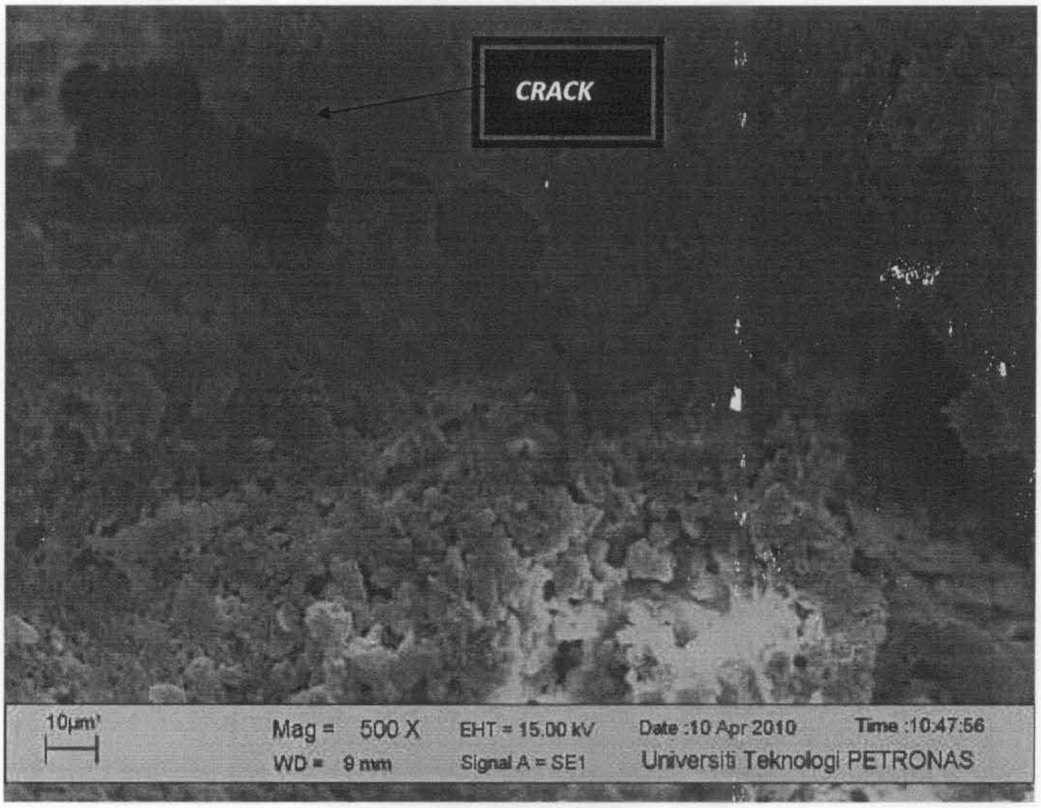
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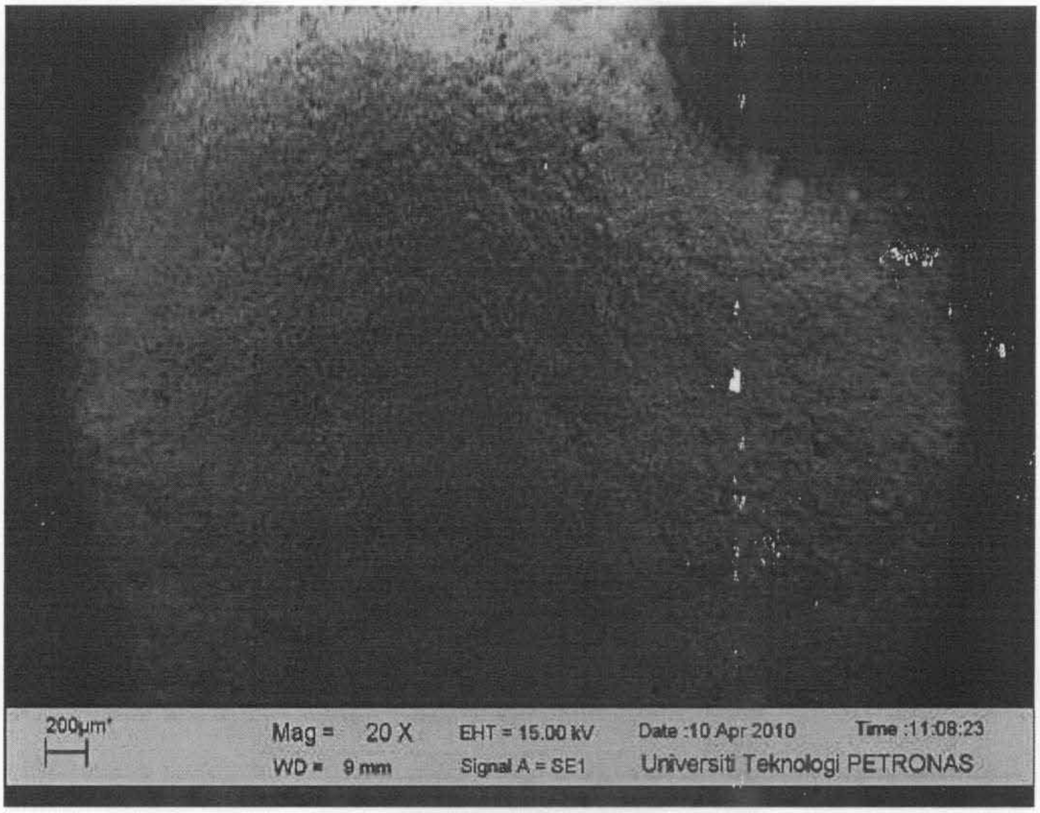
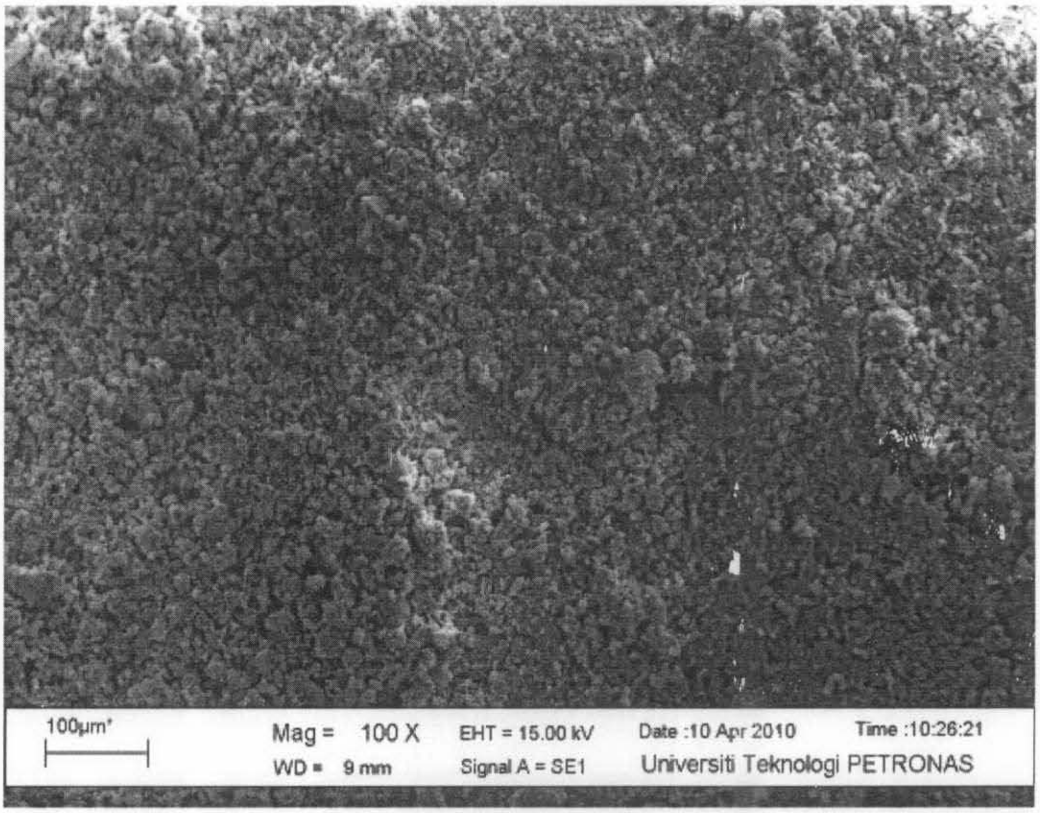


Under this curing condition, the cement cube suffers the mass loss of 9.08 %, which is lower than one cured under the temperature of 90 ^{O}F and 150 ^{O}F. White powder precipitate is found on cement cube surface after the contact with HCl. Crack ecixts on the cube surface. The chemical alteration has been disrurbed by the HCl attack. The first series of experiment is to study the effect of curing temperature towards cement resistance to HCl attack. From the observation, it storongly proves the increasing curing temperature enhance the cement resistance towards HCl attack. From the research, It is found that the increase of temperature reduces the cement permeability. As a result, the acid solubility of CaO will be significantly reduced, leading to lesser mass loss %. Temperature has pronounced positive effect on cement resistance towards HCL acid attack.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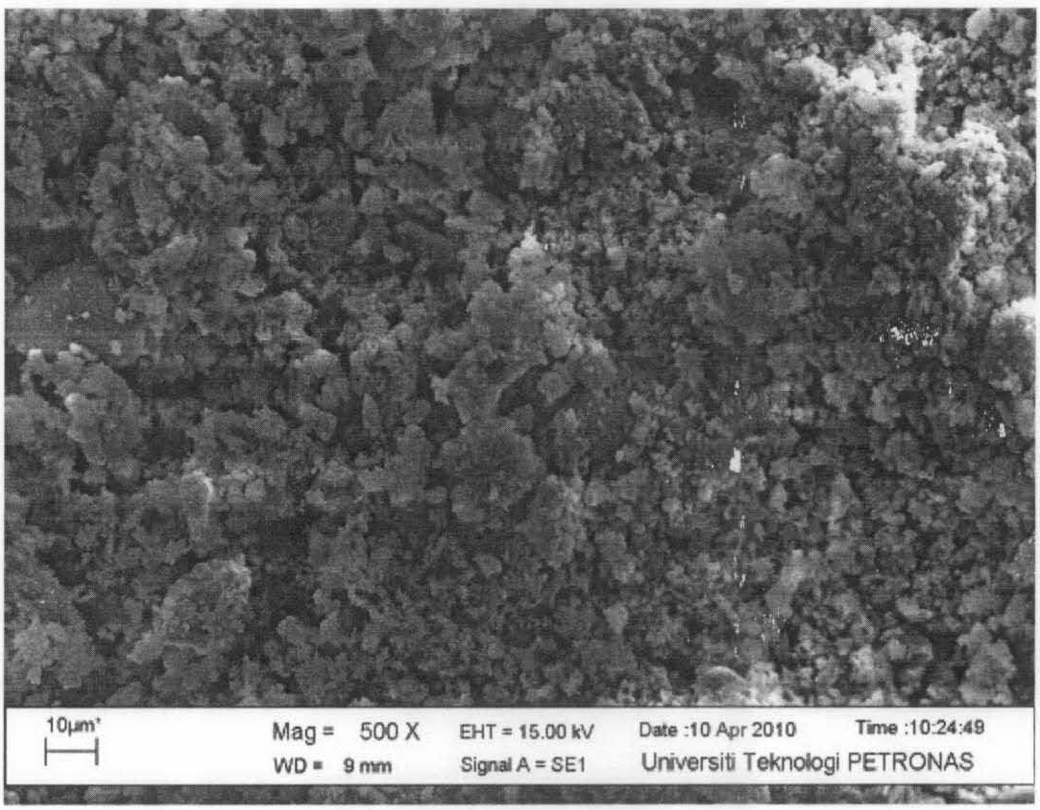
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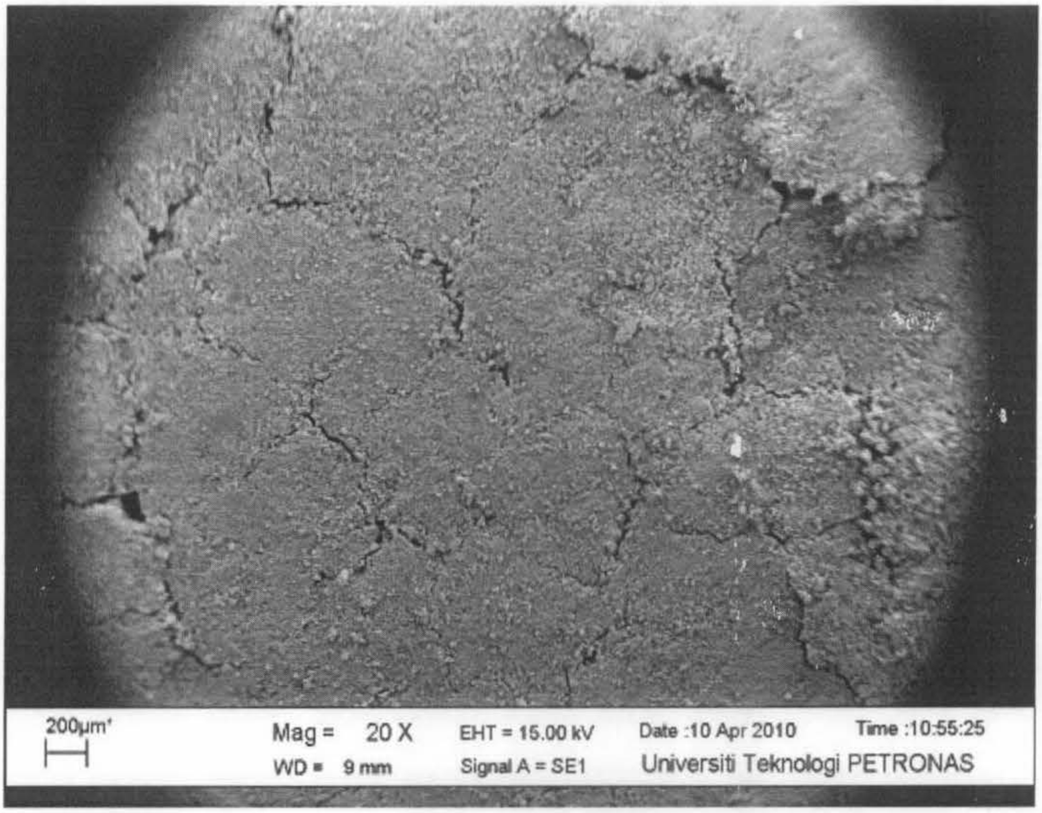
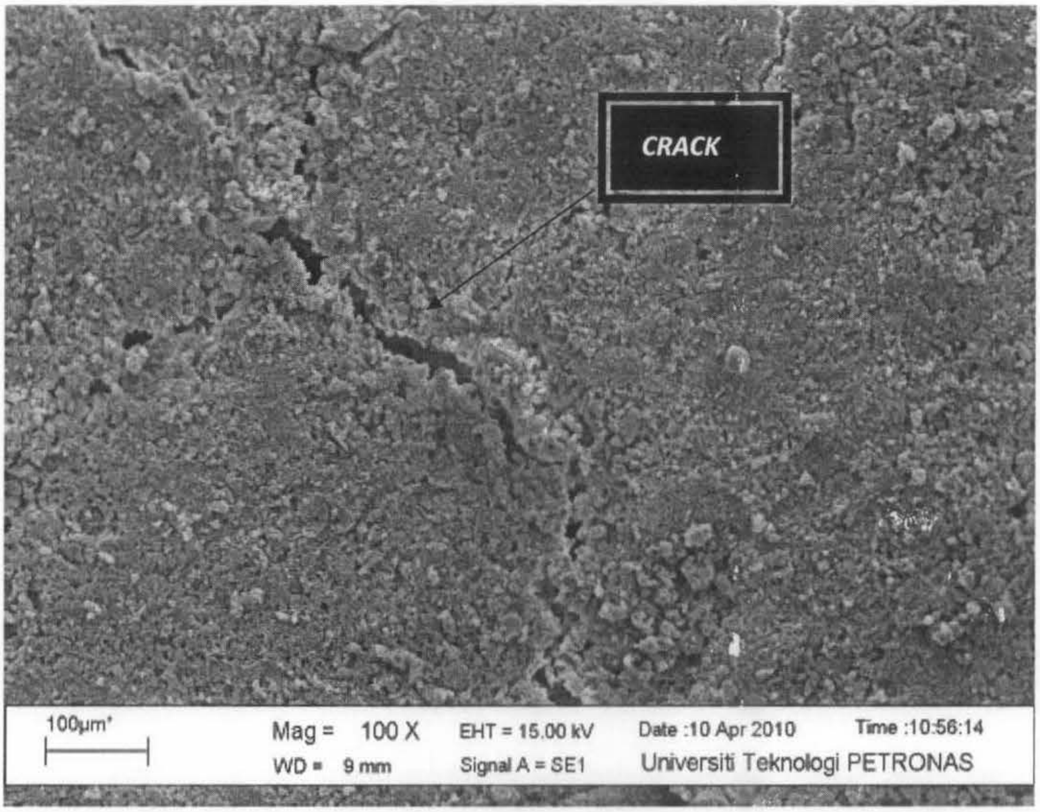
SURFACE - 4000 psi, 175 ^{O}F



Under this curing condition, the cement cube suffers the mass loss of 9.07. White powder precipitate is found on cement cube surface after the contact with HCl. Crack ecixts on the cube surface. The chemical alteration has been disrurbed by the HCl attack. This is another set of experiment to study the curing pressure effect towards cement strength development during the first 8 curing hours. With comparison with the cube cured under the same curing temperature of 175 ^{O}F but at different curing pressure of 3000 psi, this cube suffers " a little" lower mass loss. Crack is relatively small. The rise of curing pressure has a little impact to enhance the cement strength development towards HCl attack.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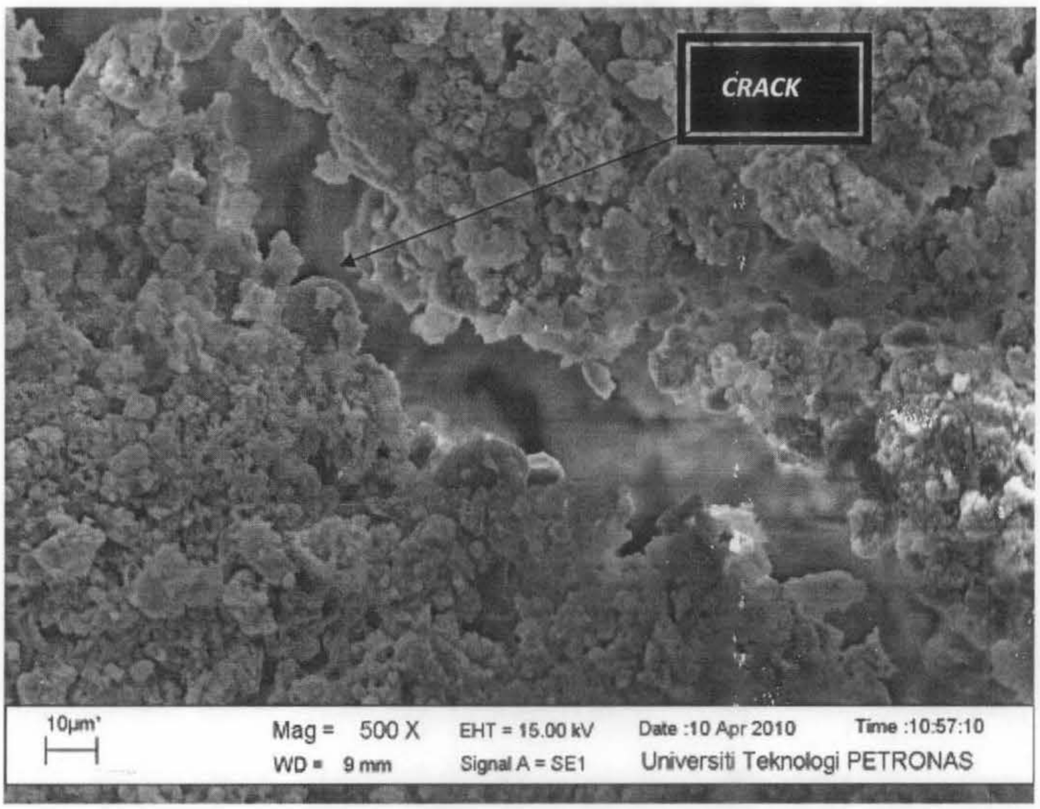
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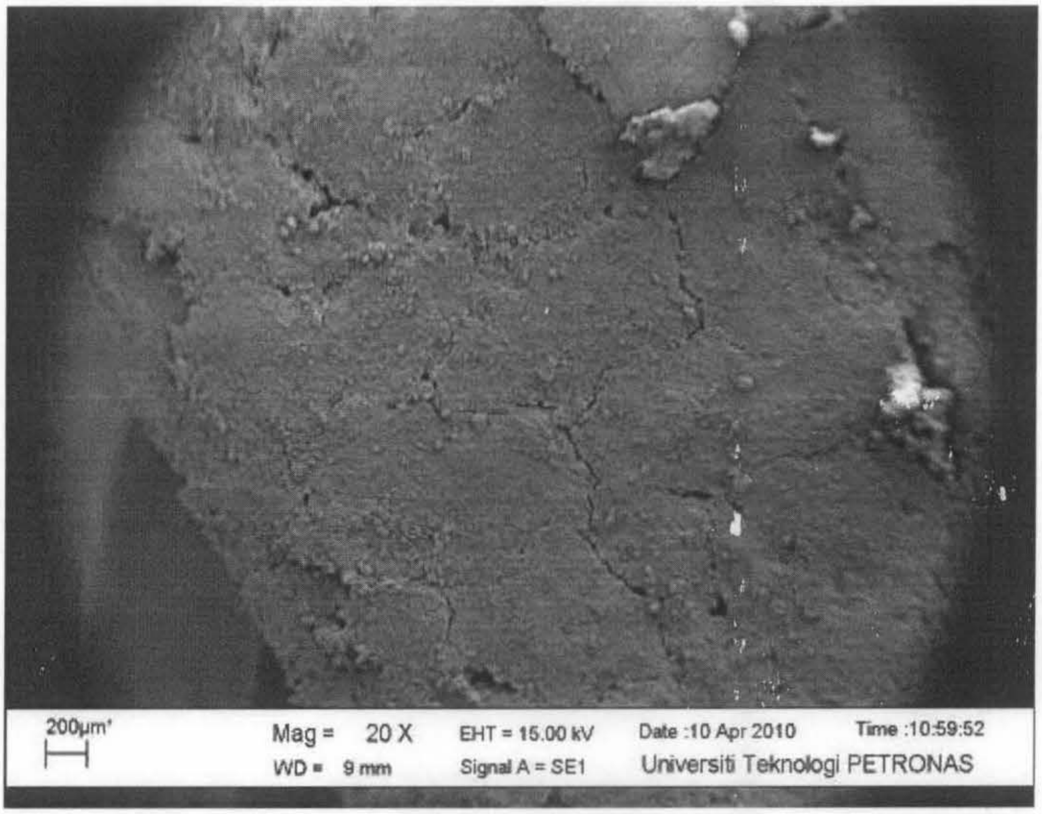
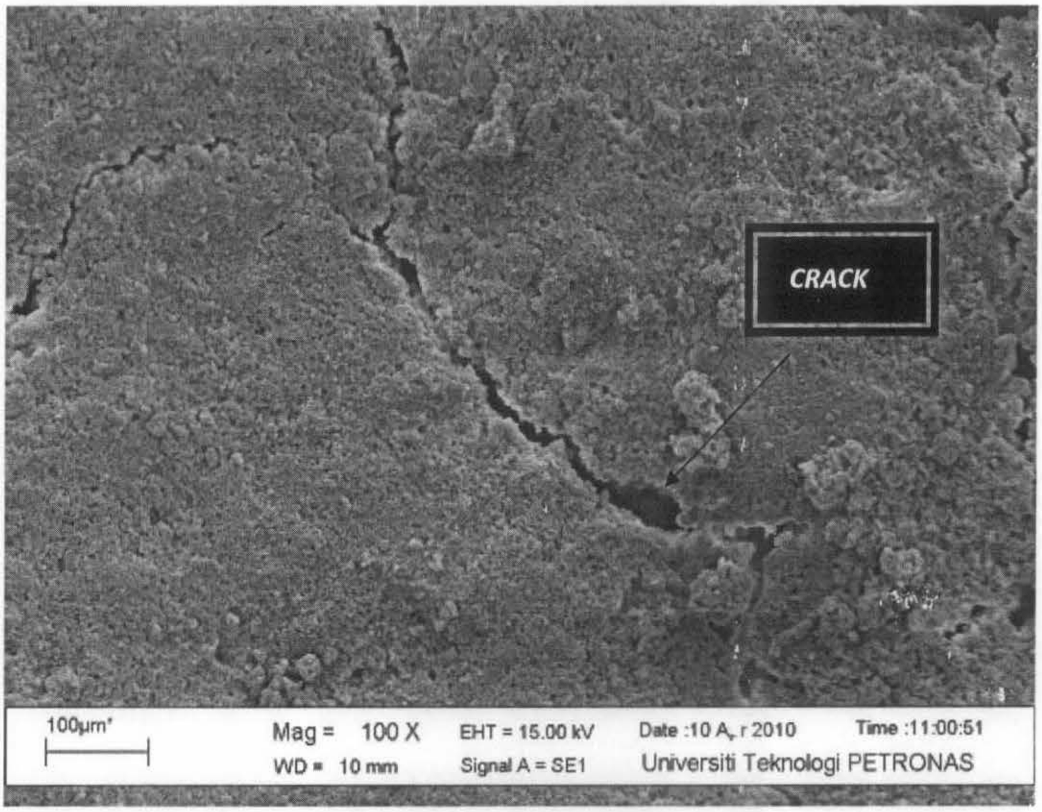
SURFACE - 5000 psi, 175 ^{O}F



Under this curing condition, the cement cube suffers the mass loss of 8.38. White powder precipitate is found on cement cube surface after the contact with HCl. Crack ecixts on the cube surface. The chemical alteration has been disrurbed by the HCl attack. It is observed that the distribution of CaO and SiO_2 crystal of higher curing temperature and pressure are more even distributed compared to lower curing condition. In other words, it indicates that the solubility of CaO and SiO_2 will decrease with increase temperature and pressure, leading to the lower amount of mass loss over the attack of HCl solution. Crack is relatively small.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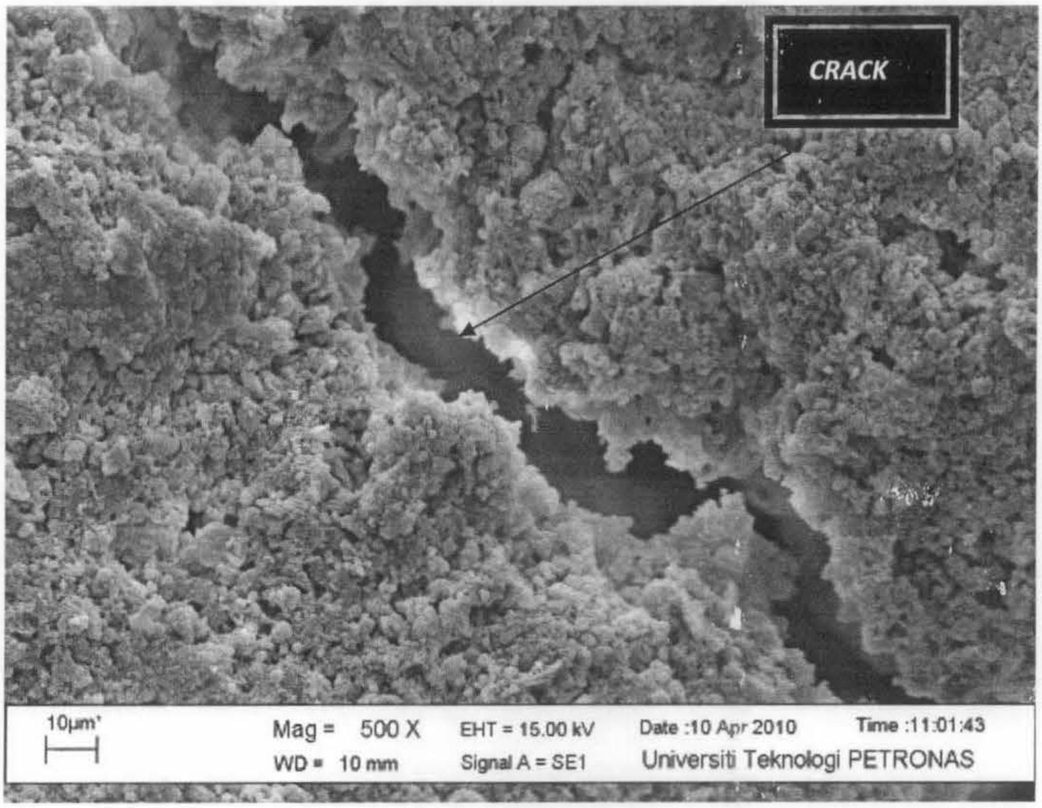
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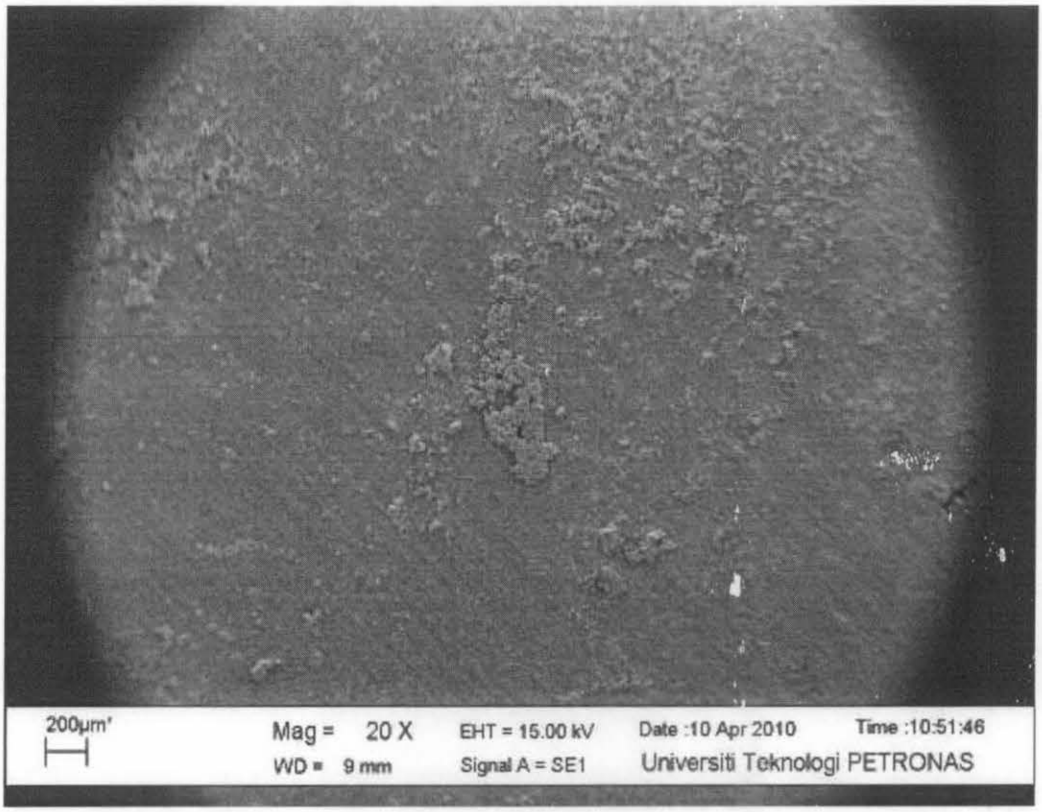
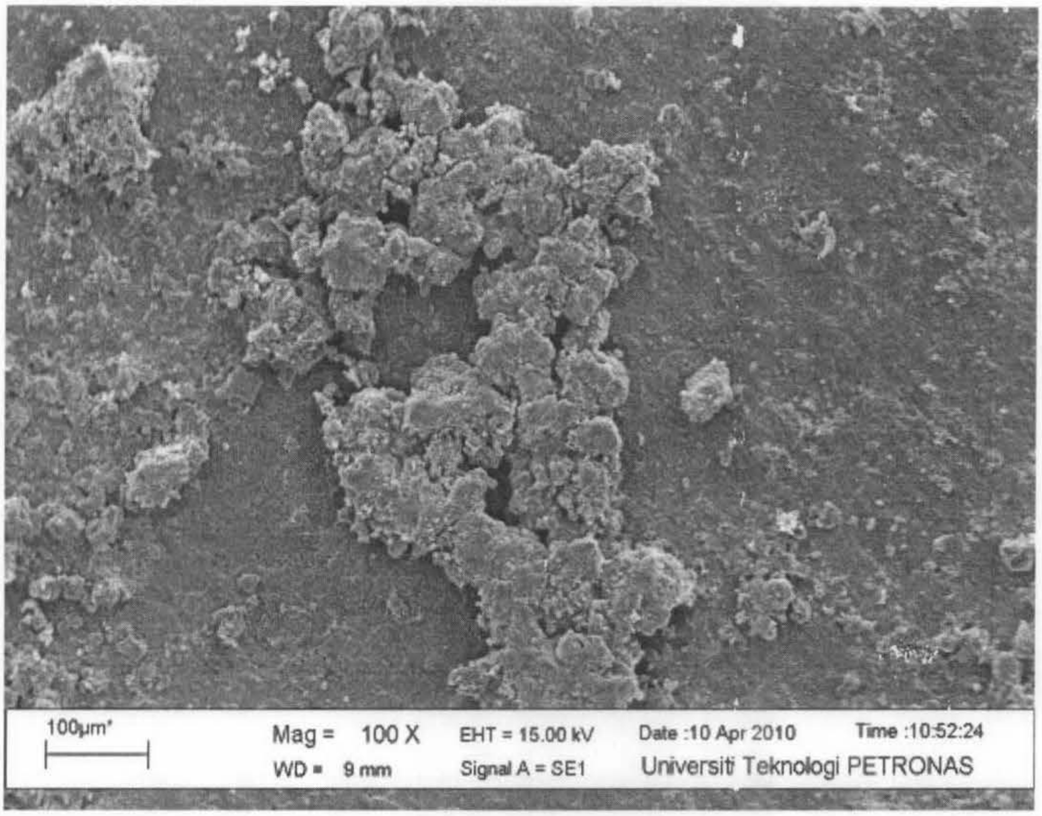
MIDDLE PART – 3000 psi, 175 ^{O}F



Beyond the 1st cut layer (3mm from surface), the cement cube surface is "clean" and free of any sign of attack, equivalent to the photomicrograph shown in reference cube. It again shows that HCl attack is a surface phenomenon. The leaching of calcium occurs only at surface.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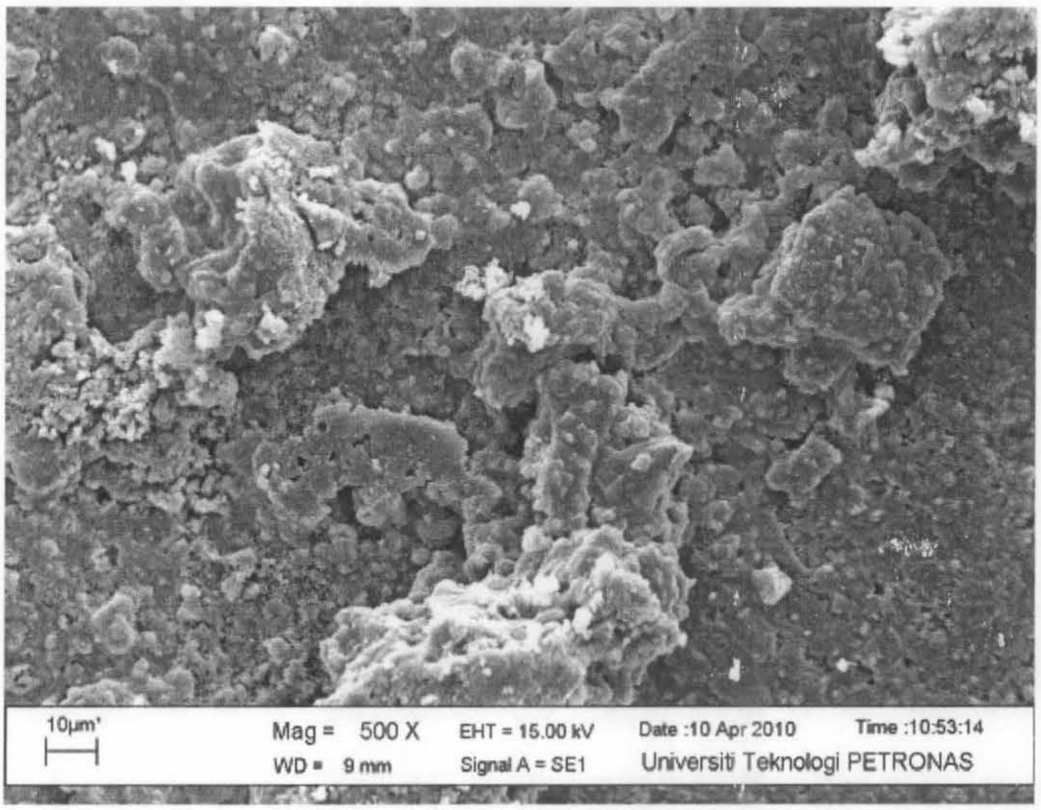
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CHAPTER 5

CONCLUSION

1. The attack on cement cube is always superficial, the material beyond the fine superficial layer maintain the same composition as the original material.
2. In the sample of cement which are attacked HCl, the white powder was found on the surface of cement, which is the product from the reaction between chlorine ion in HCl and calcium oxide.
3. The curing temperature and pressure pronounce positive impact on cement strength development during the first 8 hours of curing.
4. All the samples contacted with HCl solution suffer mass loss due to the leaching of calcium and solubility of calcium in the acid solution.
5. The lower the curing temperature, the higher the mass loss % suffered by the cement cube.
6. Curing pressure has little impact on cement strength development. Higher curing pressure contributes to higher cement resistance towards HCl attack.
7. The impact of curing temperature is far greater than curing pressure on Class G cement resistance towards HCl attack.

This study enhances the understanding of HCl attack mechanism in well-stimulating activities, enabling a better control of damage caused by Acidizing Stimulation. The permeability and integrity of the cement in the annulus and in the wellbore seal will determine how effective the cement is in preventing fluid leakage. The objectives of the study had been achieved successfully.

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Appendix

Class G Oilwell Cement

Conforms to API Specifications for Materials and Testing for Well Cementing API Spec. 10A

Chemical Requirements	**API Class G Requirements**	**Typical Lehigh Inland Performance**
MgO max %	6.0	3.6
SO_3 max %	3.0	2.5
Loss on Ign. max %	3.0	1.2
Insoluble Res. max %	0.75	0.16
C_3S max %	48 - 58	53.0
C_3A max %	8.0	2.8
Total Alkali as Na20%	0.75	0.6
Physical Requirements	**API Class G Requirements**	**Typical Lehigh Inland Performance**
Water % by wt. of cement	44.0	44.0
Soundness % max	0.8	0.09
Free water max ml	5.8	3.9
Min compr. str. MPa (8 hours) at temp. 38C, Atm. pressure at temp. 60C, Atm. pressure	2.1 10.3	3.5 15.0
Max consistency	30.0	10.0
Thickening Time (schedule 5) minimum (minutes)	90 - 120	110

The table above compares the properties of Lehigh Inland's Class G Oilwell Cement with the requirements of API Spec. 10A.

**Based on 250 ml volume, percentage equivalent of 3.5 ml is 1.4%*

Uses

Class G Oilwell Cement is intended for use as a basic well cement for surface 2,440 m (8000 ft.) depth as manufactured or can be used with accelerators and retarders to cover a wide range of well depths and temperatures.

Lehigh Inland's Class G Oilwell Cement is available in bulk or in 40 kg bags.

Specifications

Due to rigid manufacturing standards, Lehigh Inland's Oilwell Cement has increased uniformity of physical and chemical properties. Class G Oilwell Cement offers dependable performance over extreme ranges of well conditions and better compatibility with additives.

For further information on Class G Oilwell Cement, please contact your nearest Lehigh Inland Cement representative.

Important Note

Because of the chemical properties of all types of cement, it is important to be aware of the following: ***Freshly mixed cement, mortar, concrete or grout may cause skin injury. Avoid contact with skin where possible. In the event of contact, wash exposed skin areas promptly with water. If any cement or cement mixtures come into contact with the eyes, rinse immediately and repeatedly with water and get prompt medical attention.***