

## Effects of leaching on pore size distribution of solidified/stabilized wastes

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### Abstract

Chemical solidification/stabilization processes are commonly used to immobilize metals in fly ash and flue gas desulfurization (FGD) sludges and to convert these wastes into monolithic or granular materials with better handling properties and reduced permeabilities. This study evaluated the role of pore structure of solidified materials during leaching. The solidified material's initial pore structure, changes in the pore structure which result during leaching, and the effects of pore structure on leaching are discussed. It was found that pore structures varied depending upon the wastes used and the solidification mix formulations tested. After acetic acid leaching, the pore structures of samples changed remarkably. Total pore volumes and pore sizes increased. The percentage of larger pores (diameter greater than 6000 nm) increased from below 5% for before-leaching samples to above 23% for after-leaching samples. The higher the alkalinity in a sample, the greater the change of pore structure due to leaching. Changes in pore structure were primarily due to leaching of calcium hydroxide.

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### Introduction

Chemical solidification and stabilization (S/S) technology is commonly used to change potentially hazardous liquid or solid wastes into less hazardous or nonhazardous solids before they are disposed in a landfill. Wastes which are commonly solidified/stabilized include metal finishing sludges, contaminated soils, municipal incinerator ash, coal combustion residues and radioactive wastes. Solidification/stabilization processes involve the blending of cement or pozzolanic materials with the waste to create a solidified matrix in which the waste constituents are chemically bound. The result is a structurally stable product with reduced permeability and reduced metal solubility and mobility.

Solidified/stabilized fly ash and flue gas desulfurization (FGD) sludge wastes were used in this research to investigate the effects of leaching on the pore size

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distribution in a S/S waste form. Many fly ash types and FGD sludges have pozzolanic capabilities, which means that they will form cementitious products when combined with lime or cement and water at ambient temperatures [1]. Fly ash is commonly used with other S/S reagents and is typically used in lime-based S/S techniques [2].

Sample porosity and pore size distribution is very important in determining the degree of leaching that will occur in a waste. The pozzolanic reactions create a calcium-silicate-hydrate (C-S-H) gel that hardens into thin, densely-packed, silicate fibrils which grow and interlace. As the water in the mix reacts with the lime and fly ash or FGD sludge, small pores, often of capillary size, are left behind. The amount and size distribution of these pores is dependent on such factors as the water/cement ratio (excess water will produce a higher porosity) and the rate of reaction. Cement-based matrices have permeabilities ranging from  $10^{-5}$  to  $10^{-9}$  cm/s, while pozzolanic materials usually range from  $10^{-6}$  to  $10^{-7}$  cm/s [3].

The rate of leaching of metals from the porous S/S waste is highly dependent on its porosity, since leaching is largely controlled by the amount of available surface area and the rate of diffusion of metals through the pore water. Leaching is a process in which the contaminants in the solid phase are transferred to the liquid phase in contact with it. Therefore, the area of the interface between the solid and the liquid in the pores is very important. Pores in the solidified matrix are dominated by capillary pores and gel pores [4]. The capillary pores are the remnants of water-filled space that exist between the partially hydrated grains, and have a pore size range from 10 nm (0.01  $\mu\text{m}$ ) to 10  $\mu\text{m}$ . The gel pores are included in the volume occupied by calcium silicate hydrate compounds, which have a range of pore sizes of 10 nm or less [4]. Many of these pores are initially filled with precipitated lime from the hydration reactions. As leaching progresses, the lime deposited in the pores and other major components of the solid matrix leach out and leave larger, or produce new, voids in the solids. Hence the microstructure of the solidified waste changes during leaching. The increase of the pore volume and pore size may significantly affect the leaching process.

The purpose of this study was to obtain a better understanding of the role of pore structure of solidified materials in the leaching process. The solidified material's initial pore structure, changes in the pore structure which result during leaching, and the effects of pore structure on leaching are discussed.

## **Methods and materials**

Solidified/stabilized samples of fly ash and flue gas desulfurization (FGD) sludge were made by mixing them with lime and water and allowing them to cure. A 90 day sequential leaching test was conducted on ground solidified samples. Leachate and solids were sampled during the leaching period for anal-

ysis. The pore structures of these solidified samples before and during leaching tests were investigated by mercury intrusion porosimetry, by gas volume displacement and by nitrogen adsorption. Following is a brief description of the study, with emphasis on the pore structure evaluation.

#### *Waste sources*

Four types of waste were used for this study: FGD sludge, two types of fly ash and LIMB ash (from the Lime Injection Multistage Burner process). Flue gas desulfurization sludge and fly ash were obtained from the Conesville Power Station, Columbus Southern Power Co. Fly ash #4 came from boiler #4 and fly ash #6 from boiler #6. This station burns Ohio coal with a typical sulfur content of 3.5% (w/w) or greater. The Conesville Station FGD system is a lime-based wet scrubber operating on units 5 and 6. The LIMB ash was collected from the Edgewater Station, Ohio Edison, in Lorain, Ohio. The LIMB process is an alternative sulfur removal system now under development. The process involves the injection of lime or limestone slurry at the top of the boiler. The calcium in the lime quickly reacts with the sulfur dioxide forming a dry ash similar to fly ash, which can be removed either by electrostatic precipitators or fabric filters. The LIMB ash is a mixture of fly ash, unreacted calcium oxide and calcium sulfate [5].

#### *Solidified sample preparation*

Wastes were solidified according to ASTM C305-82 and ASTM C192-90. A series of mixtures of the wastes, Type N hydrated lime and deionized water were prepared and screened for suitability. Four mixtures were selected for the leaching tests. These are shown in Table 1. Mixture B is the formulation used by the Conesville Station for its FGD sludge and fly ash, mixture A is our optimized mixture for those wastes, mixture C is an optimized mixture for fly ash #6 alone, and mixture D is the best mixture from the screening process for the LIMB ash. All samples were cured for a minimum of 28 days before leach testing began.

TABLE 1

Mixture formulations chosen for leaching studies

Mixture	Composition	Unconfined compressive strength (psi)
A	45% FGD, 50% FA #4, 5% Lime	230
B <sup>a</sup>	55% FGD, 43% FA #6, 2% Lime	73
C	72% FA #4, 10% Lime, 18% Water	1055
D	90% LIMB, 10% Water	1164

<sup>a</sup>Formulation used at Conesville station.

### *Leaching tests*

Leaching tests were conducted using both deionized water and 0.01 N acetic acid leachant. Leaching tests followed a modified ANSI/ANS 16.1 multiple leaching procedure. Solidified samples were ground to a size between 4.8 mm and 9.5 mm, then placed in the appropriate leachant. Deionized water leached samples had liquid/ solid (*L/S*) ratios of 4/1, 20/1 or 100/1; acetic acid leached samples had a *L/S* of 20/1. The leachants were changed on days 1, 3, 5, 7, 14, 28, 45, and 90.

Leachate samples were taken at each leachant change. Analyses on leachate samples included pH, alkalinity, acidity (for acid leaching samples only), total dissolved solids, metals and oxidation-reduction potential.

Detailed information about the above mentioned methods can be found elsewhere [5].

### *Microstructure investigation*

The effect of leaching on the microstructure of solidified wastes was investigated by measurement of pore size distribution using mercury intrusion porosimetry. The Micromeritics Model 9310 Poresizer was used for the determination of pore volume, pore size distribution, bulk density and skeletal density. In addition, the skeletal density (or true density) and the surface area were measured by the gas volume displacement method using a helium pycnometer (Micromeritics Pycnometer Model 1305) and by the nitrogen adsorption method using a surface area analyzer (Monosorb, Model-MS-12, Quantachrome Corporation).

Mercury intrusion analysis was conducted on solidified waste samples before leaching; after 45 and 90 days deionized water (D.I.) leaching; and after 14, 45, and 90 days of acid leaching. Due to the limited amount of solids available, triplicate tests were carried out only for unleached samples and wastes after 90 days D.I. leaching with a leachant/solid ratio of 20/1. Samples for analysis were dried in an oven at 105°C and then kept in a vacuum desiccator.

## **Results**

### *Pore structure of solidified samples before leaching*

Figure 1 shows a comparison of cumulative intrusion volumes for the four mixes evaluated before leaching (see Table 1 for mixes). Measurements of pore size distribution on samples before leaching were conducted in triplicate; the results presented are the mean values. Mixture B, the formulation used at the Conesville Station, has the highest total intrusion volume, while mixture C has the lowest. Mixtures A and D have almost the same total intrusion volume, as well as the same curve shape.

The dominant pore size for each mixture can be found in Fig. 2, a bar graph showing the incremental intrusion volumes at different pore diameters. For

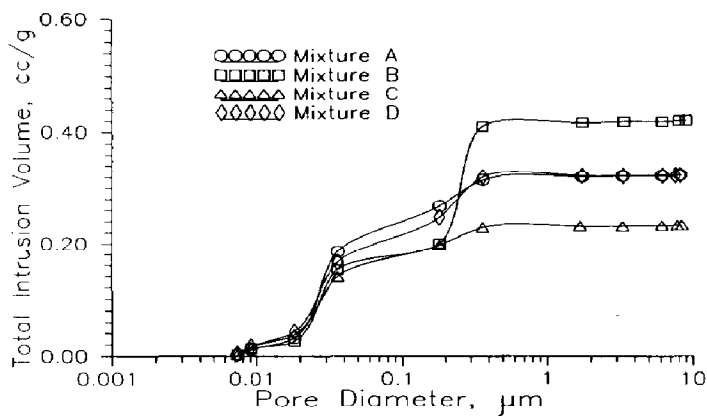


Fig. 1. Comparison of cumulative total intrusion volumes before leaching of the four waste mixtures evaluated.

comparison purposes, the incremental intrusion volume at each diameter is normalized to the total intrusion volume and expressed in percentage on the vertical axis. For all four mixtures, most of their pore volumes were contributed by pores with diameters of 36 nm to 360 nm. Except for mixture B, all the mixtures have a typical Gaussian pore size distribution.

The differences in porosity among the four mixtures may have been caused largely by the differences in water/lime ratios. Table 2 lists the total intrusion volume of the mixtures and the mixtures' water/lime ratio. The water/lime ratios were calculated from the formulation of the mixtures and the original waste characteristics.

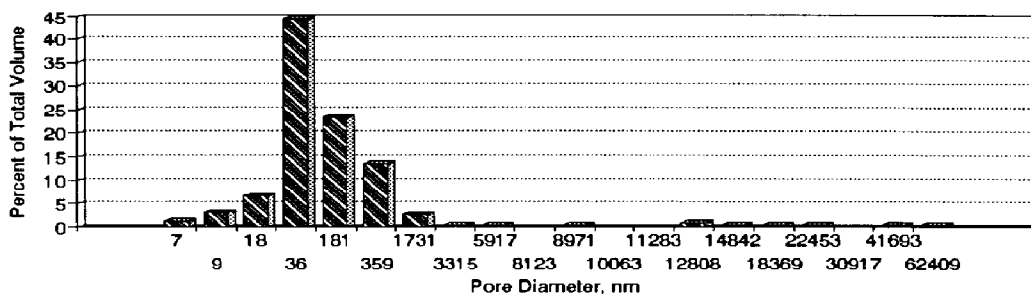
As shown in Table 2, a good agreement between pore volume and water/lime ratio exists for mixtures A, B, and C. The pore volume appears to be equal to one-half the water/lime ratio, with the exception of mixture D. Since mixture D is made of materials obtained from a different source and of different composition, its inconsistency with the above mentioned behavior is understandable.

#### *Effect of leaching on pore structure*

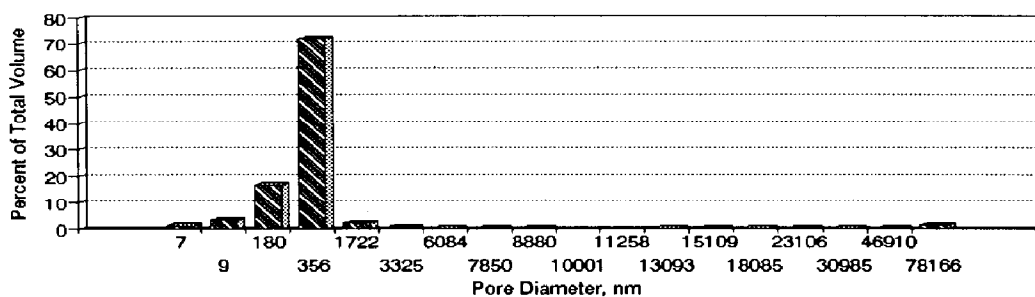
The results of mercury intrusion measurements on waste samples after 90 days deionized water leaching and 0.01 *N* acetic acid leaching are presented in Figs. 3 through 6. As expected, the pore structure of the wastes did not change significantly due to D.I. leaching, but changes in pore structure were very noticeable during acid leaching. After acid leaching, the major pore size shifts from 36 nm to 3300 nm for mixtures A, B, and D, and from 36 nm to 1700 nm for mixture C (see Figures 7-10). The percentage of the larger pores (diameter > 6 μm) increased and the percentage of the smaller pores (diameters < 36 nm) decreased, as shown in Table 3.

The increase in pore volume is probably due to the enlargement of the orig-

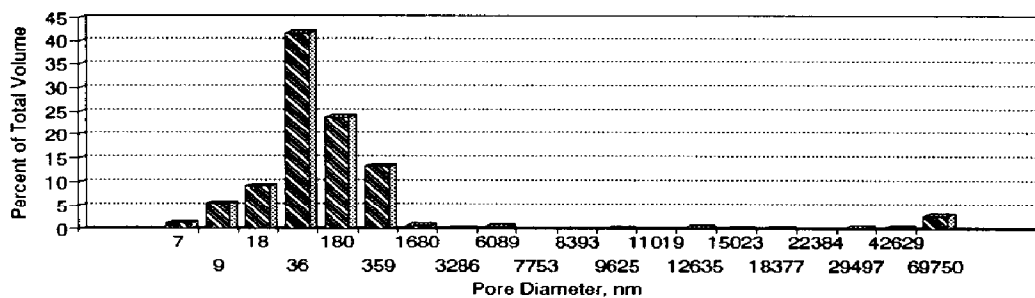
Mix A, before leaching



Mix B, before leaching



Mix C, before leaching



Mix D, before leaching

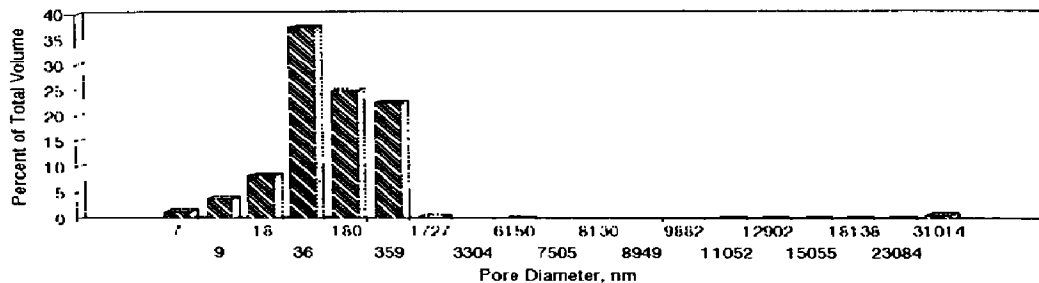


Fig. 2. Incremental intrusion volumes of the four mixes before leaching.

TABLE 2

Pore volume and water/lime ratio for various S/S waste mixtures

Mixture	Pore volume (cm <sup>3</sup> /g)	Water/lime ratio
A	0.3360	0.7001
B	0.4293	0.8610
C	0.2432	0.5242
D	0.3356	0.3287

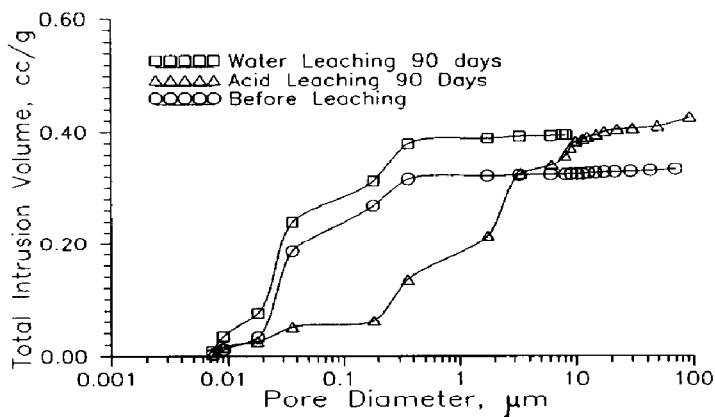


Fig. 3. Comparison of the effect of D.I. leaching and acetic acid leaching on solidified samples, mixture A.

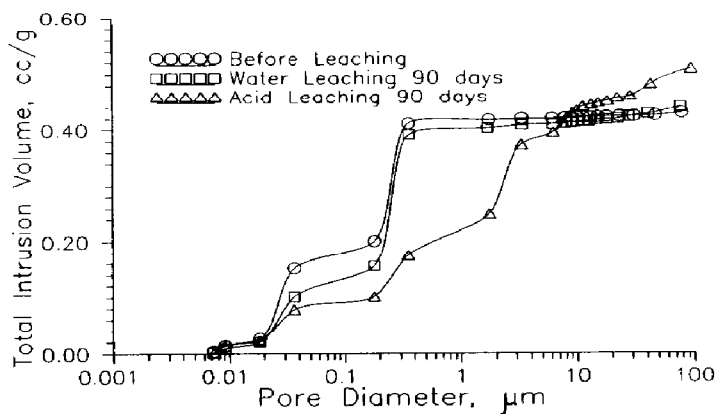


Fig. 4. Comparison of the effect of D.I. leaching and acetic acid leaching on solidified samples, mixture B.

inal pores due to the leaching of calcium hydroxide, resulting from the attack of hydrogen ions in the leachant, and to development of access routes to previously occluded pores.

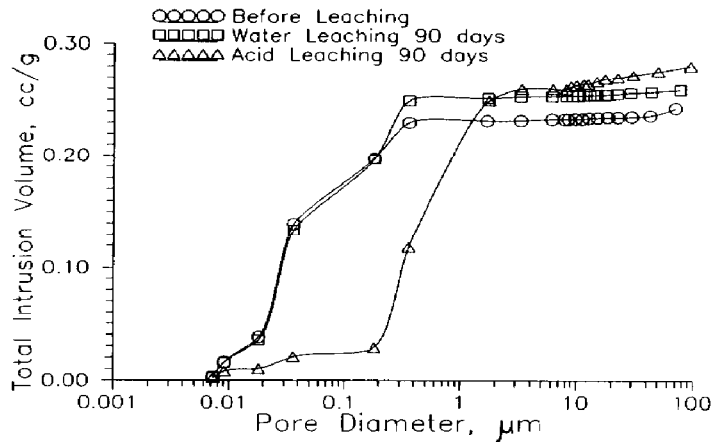


Fig. 5. Comparison of the effect of D.I. leaching and acetic acid leaching on solidified samples, mixture C.

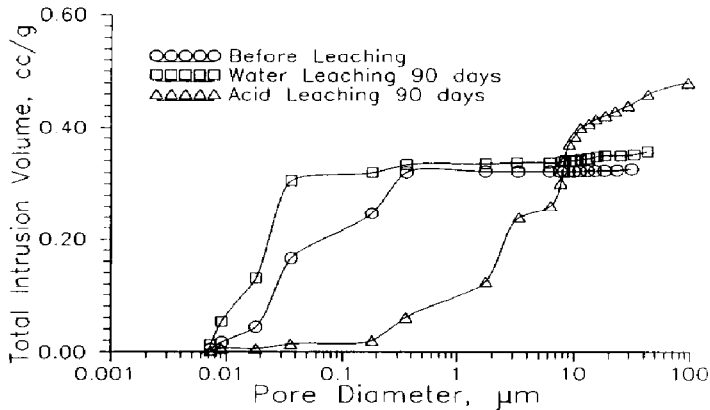


Fig. 6. Comparison of the effect of D.I. leaching and acetic acid leaching on solidified samples, mixture D.

The relationship between the change in pore size distribution and the leaching of alkalinity is also demonstrated by investigating the effect of leaching time on the pore structure of the mixtures. Figures 11 through 14 compare the cumulative intrusion volume curves before leaching, after 45 days acid leaching (after 14 days acid leaching for mixture B) and after 90 days acid leaching. The curves for mixtures A and C are not statistically different between 45 days leaching and 90 days leaching. For mixture D, however, the curves for 45 days leaching and 90 days leaching are remarkably different. This is probably because all of the available calcium hydroxide in mixtures A and C has leached out within the first 45 days so that their pore structures are not affected by the leaching for the rest of the test. This is supported by the results of consumed acidity measurements on the leachate. For mixtures A and C, the cumulative consumed acidity curves reached their original alkalinity levels before 45 days



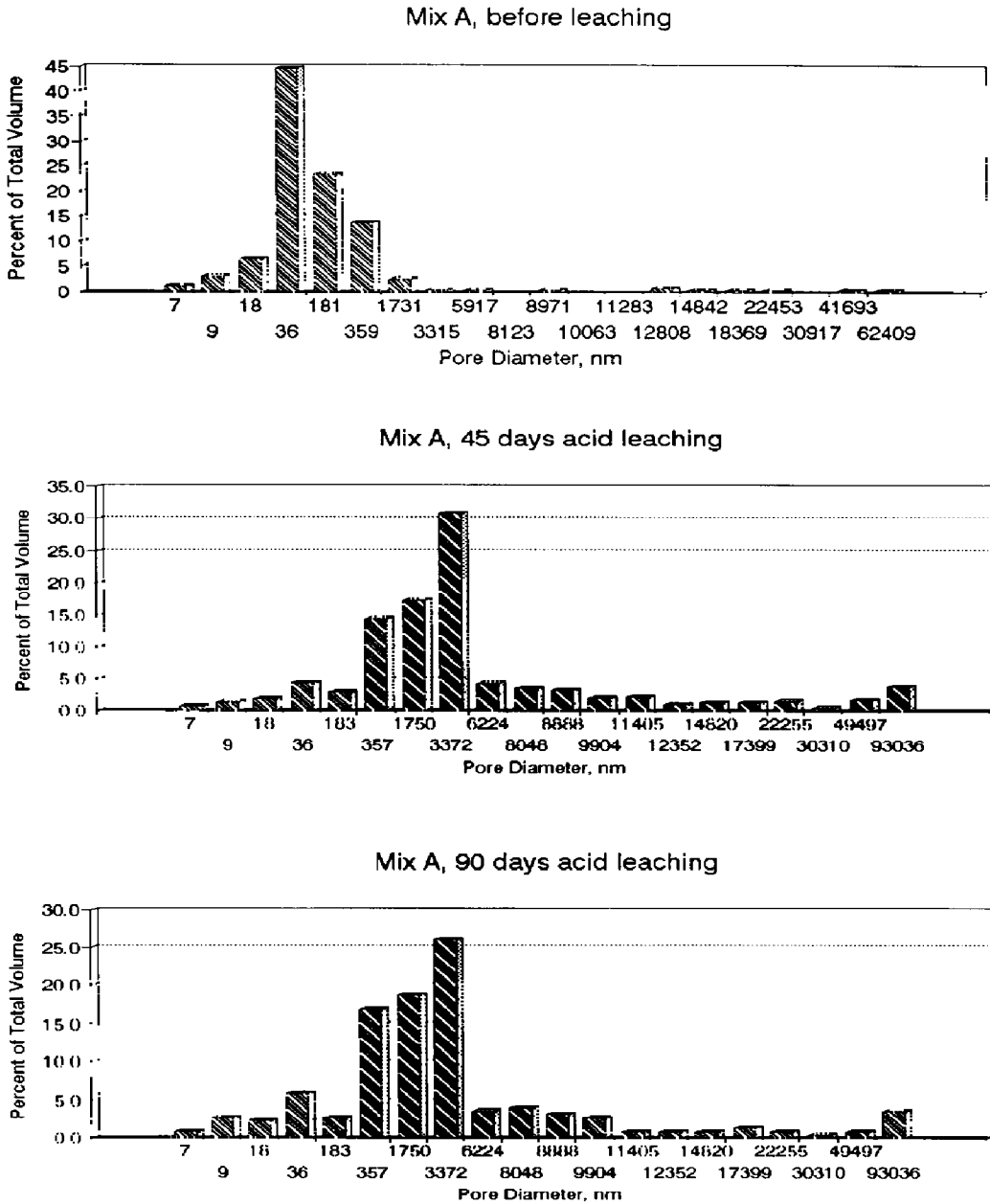


Fig. 7. Effect of acetic acid leaching on pore size distribution of mixture A after various leaching periods.

leaching. However, the acidity-consumed curve for mixture D is still not below its original alkalinity level, even after 90 days leaching; therefore, the structure of mixture D could continue to change. Mixture B samples did not retain their physical integrity and broke down into smaller pieces over the 90 day leaching period. Therefore, their results cannot be compared with the other mixes.

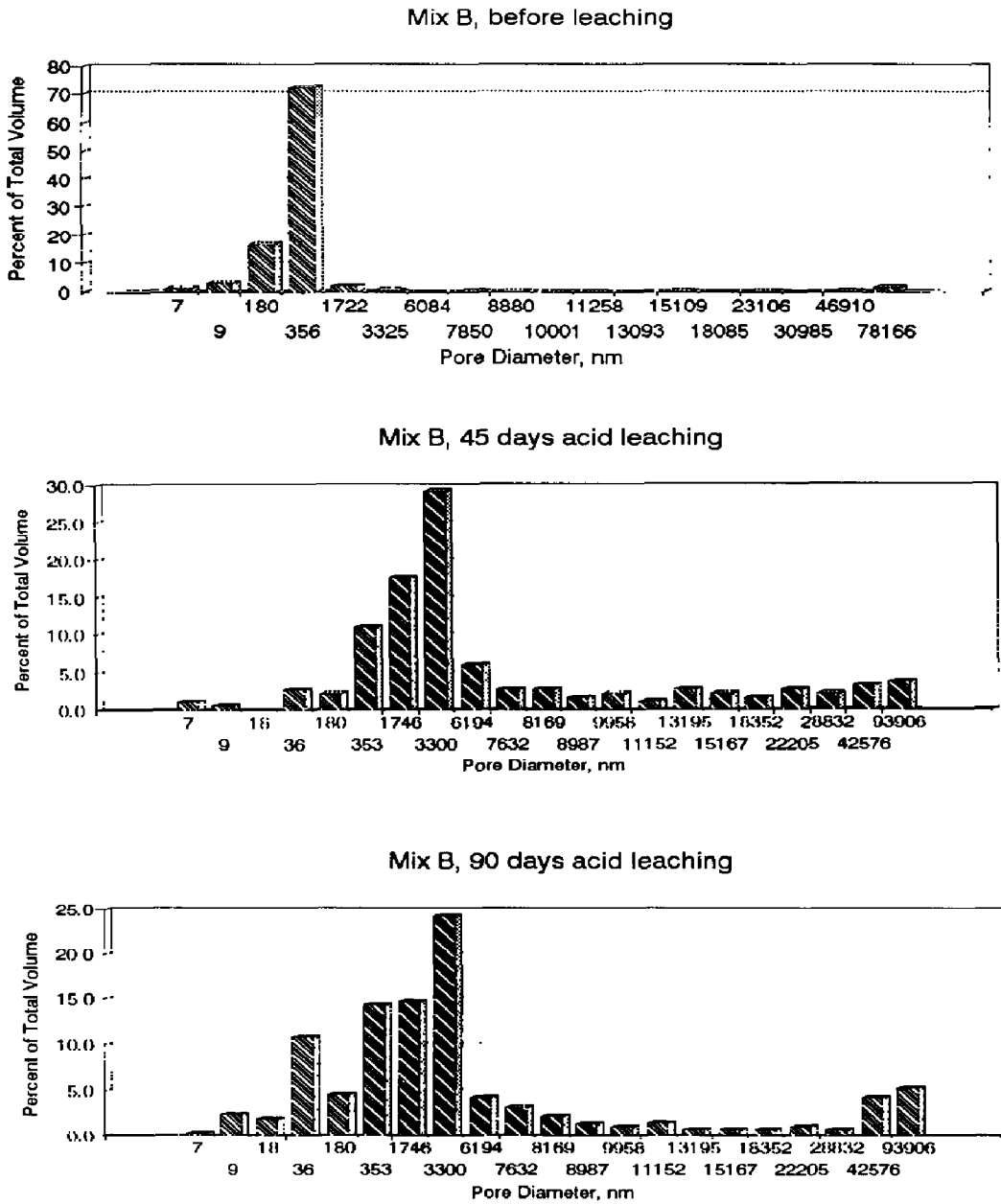


Fig. 8. Effect of acetic acid leaching on pore size distribution of mixture B after various leaching periods.

The higher the alkalinity of a waste, the greater the pore structure of the waste will be changed through a leaching process. Since mixture D has the highest alkalinity among the four mixtures, the continued change of the pore structure due to the release of calcium hydroxide from the solid matrix into the leachate is reasonable. It is also noticed that the total intrusion volume at the

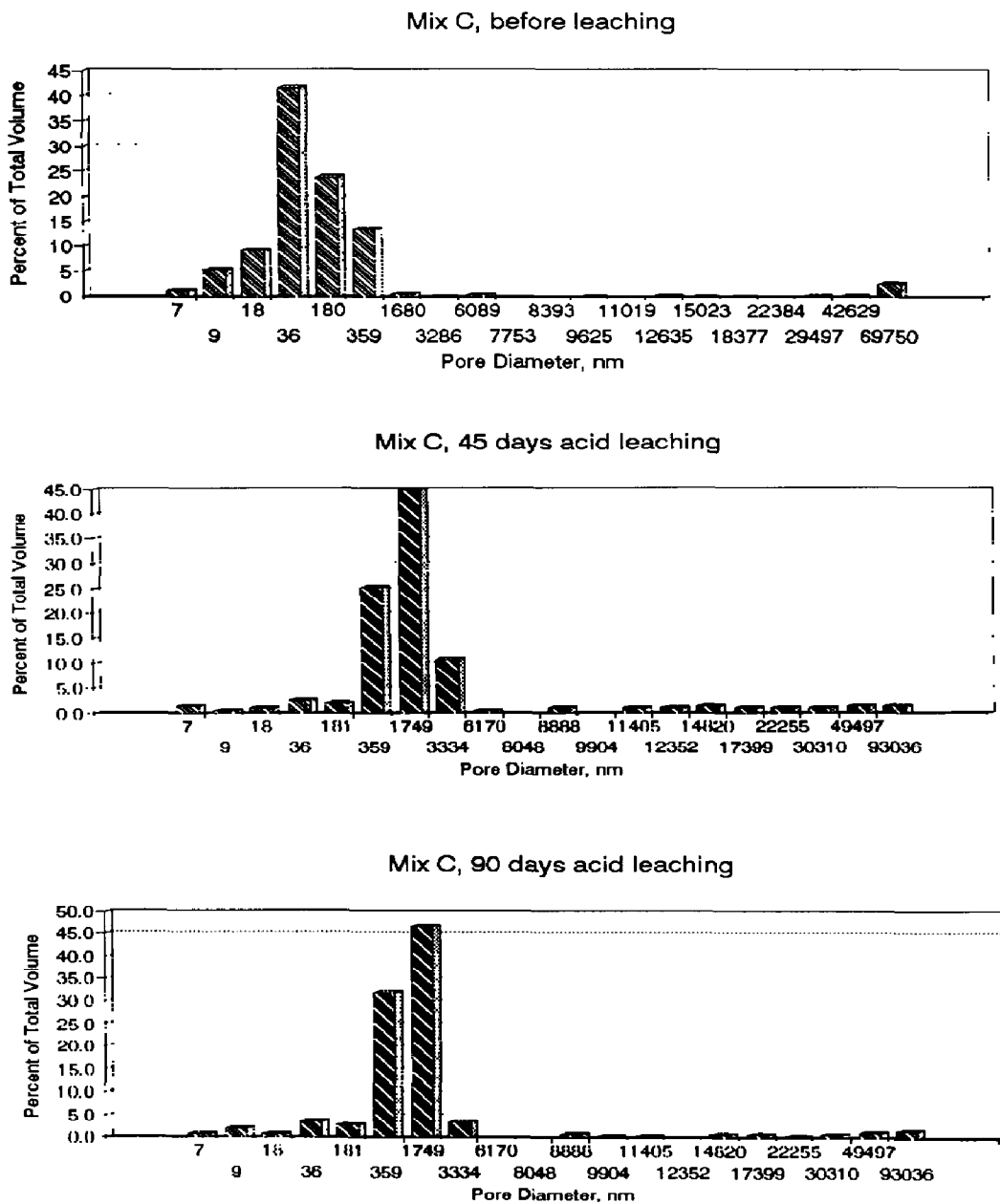


Fig. 9. Effect of acetic acid leaching on pore size distribution of mixture C after various leaching periods.

end of the leaching test is slightly less than that at the early stages of the leaching test for mixtures A, C, and D. More information will be needed to understand this behavior. It may involve the destruction of C-S-H structure, or possibly the blocking of pore openings by the production of deposited compounds.

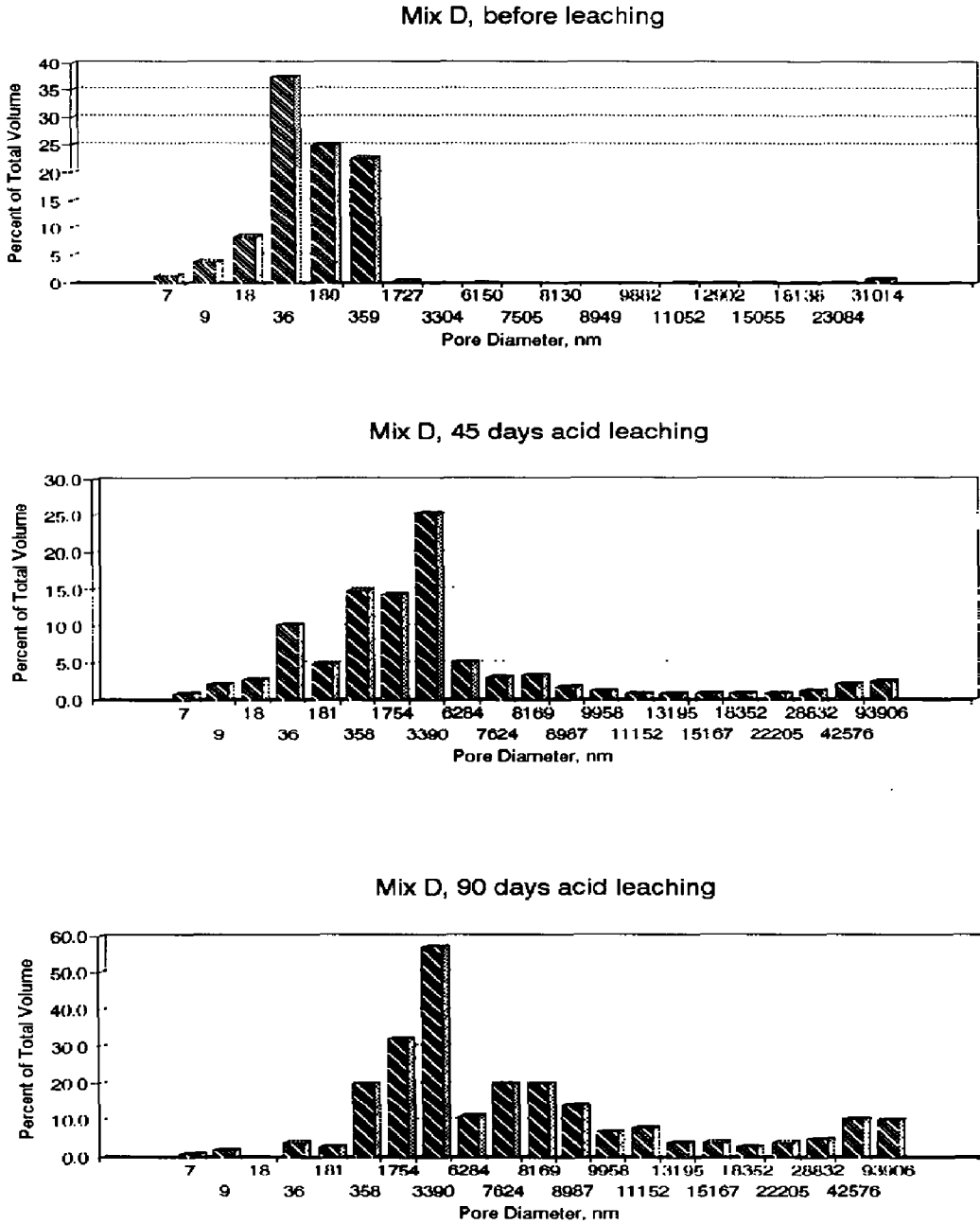


Fig. 10. Effect of acetic acid leaching on pore size distribution of mixture D after various leaching periods.

*Effect of pore structure on leaching*

According to leaching test results, mixture B is ranked as the worst solidified waste mix, while mixture C is the best in terms of the metal leaching. According

TABLE 3

Comparison of pore size ( $d$ ) distribution for samples before leaching and after 90 days acid leaching

Pore size (nm)	Pore volume/total uptake (%)	
	Before leaching	After leaching
<i>Mixture A</i>		
$7.3 < d < 36$	9.72	5.94
$6000 < d$	3.18	23.74
<i>Mixture B</i>		
$7.3 < d < 36$	6.09	4.58
$6000 < d$	2.37	26.40
<i>Mixture C</i>		
$7.3 < d < 36$	15.67	3.67
$6000 < d$	4.62	7.38
<i>Mixture D</i>		
$7.3 < d < 36$	8.22	1.25
$6000 < d$	1.42	50.21

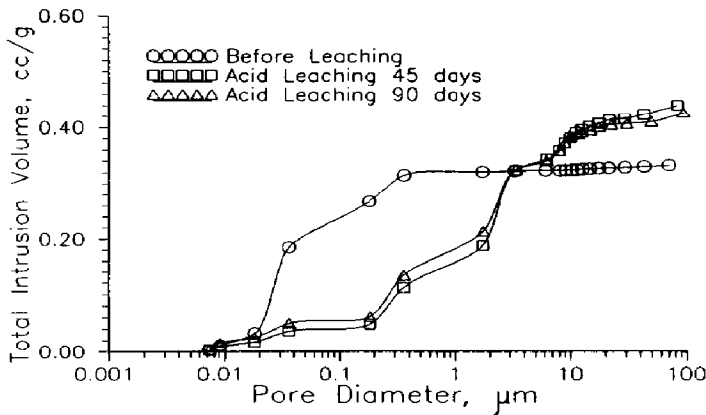


Fig. 11. Effect of acid leaching time on total intrusion volume of solidified mixture A.

to mercury intrusion measurements, as demonstrated above, mixture B had more pore volume than the other mixtures and mixture C had the lowest pore volume. The more porous a mixture is, the easier it is for the leachant to reach the reaction site; therefore, more of the metals can be leached out. Metal fixation and leaching are very complicated processes and cannot be explained just by the porosity, but the porosity of the solidified waste can be one of the major contributing factors.

The effect of pore structure on leaching may be due not only to the initial pore structure characteristics, but may also be affected by changes in pore structure during leaching. Although mixture D had a similar initial pore volume and size distribution as mixture A, a greater pore structure change oc-

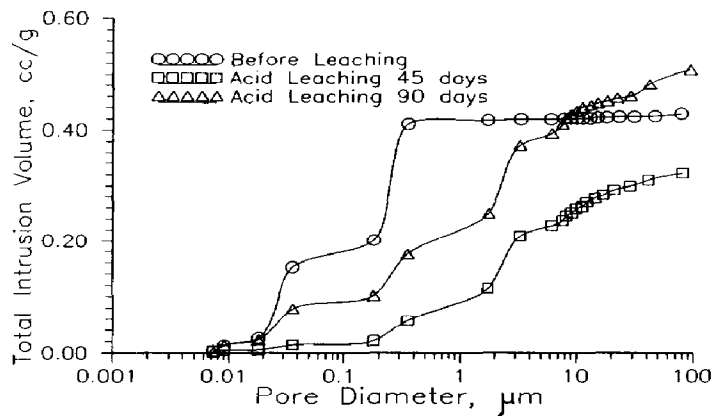


Fig. 12. Effect of acid leaching time on total intrusion volume of solidified mixture B.

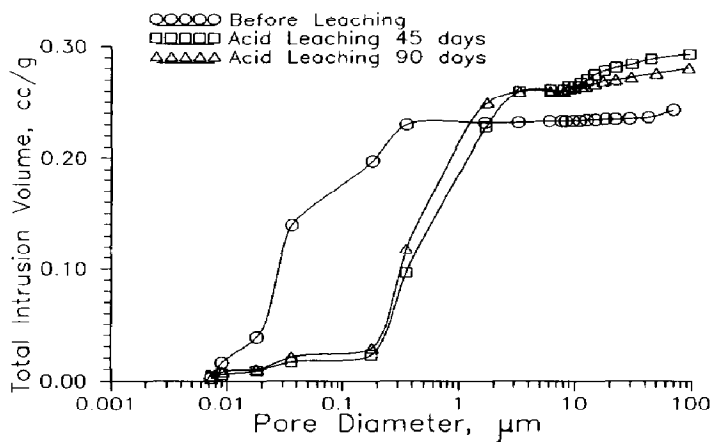


Fig. 13. Effect of acid leaching time on total intrusion volume of solidified mixture C.

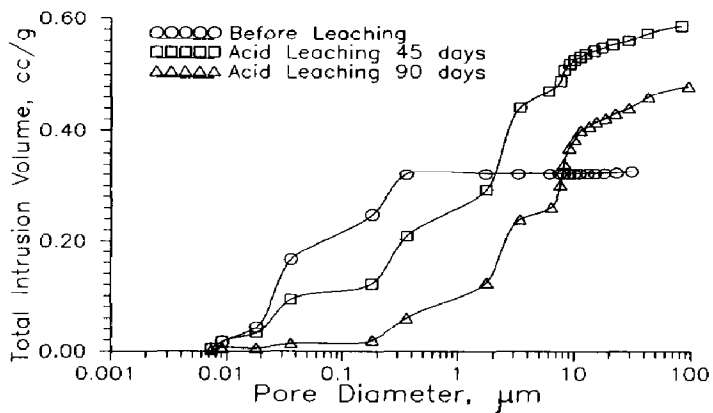


Fig. 14. Effect of acid leaching time on total intrusion volume of solidified mixture D.

curred to mixture D during the water and acid leaching, with the total intrusion volume increasing by almost 50%. Therefore, it is not surprising to find that mixture D was ranked as the second worst solidified waste mix, based on metal leaching, especially for the metals which are probably precipitated with the calcium hydroxide in the pores.

#### *Data reliability*

Due to the heterogeneous character of these samples, variations in results are expected. In order to know whether the change of pore structure measured in this study is significant compared to the variation of results caused by measurement errors, triplicate tests were conducted on some after-leaching samples. In all cases, the standard error was less than 10%. These results indicate that analytical and sampling variability were minimal.

It should be pointed out that the reliability of pore structure evaluation is limited by the available test methods. Mercury intrusion methods have some inherent chances for misinterpretation. Pore structure can be destroyed during the drying stage that is necessary for the preparation of samples. Since the measurement method is based upon the assumption that the pore has a cylindrical shape, and the real pore structure probably has a far more complex shape, the measured results may not reflect the real situation. In addition, the existence of "ink bottle shape" pores would cause mismeasurements.

#### **Summary and conclusions**

Different pore structures were observed for the four formulations of our solidified samples. Mixture C had the lowest pore volume and the least leaching potential, while mixture B had the highest pore volume and the largest leaching potential.

After acetic acid leaching tests, the pore structure of samples changed remarkably. Total pore volumes and pore sizes increased. The percentage of larger pores ( $d > 6000$  nm) increased from below 5% for before-leaching samples to above 23% for after-leaching samples. The higher the alkalinity in a sample, the greater the change of pore structure due to leaching. Changes in pore structure of solidified samples were most likely caused by the leaching of calcium hydroxide. No significant pore change was observed for mixtures A, B, and C after the alkalinities of those samples were consumed.

#### **Acknowledgement**

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