

Leaching characteristics of a model solidification/ stabilization system: Tricalcium silicate and copper oxide

Cheng-Fang Lin*, Teng-Hung Huang

Graduate Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan, 106, ROC

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Abstract

The major cement constituent, i.e. tricalcium silicate (C_3S), and copper oxide were used in this study as a model solidification/stabilization system for investigating the leaching characteristics of a solidified waste form. The semi-dynamic leaching process was employed for simulating the dynamic nature of the relevant conditions. The primary objective of this work lies in assessing the long-term stability of a waste matrix which would experience acidic leaching at a disposal site. The changes in the matrix constituents, pore size, pore volume, physical strength, as well as the pH of the matrix were closely related with each other for interpretation of the leaching mechanism. The dissolution of calcium compounds was found to be critical to the leaching of solidified hazardous materials. Dissolution of calcium compounds in the matrix would increase the number of pores and pore size and, therefore, enhance the dissolution reactions and solute transport within the matrix. Dissolution of the hydration products was promoted by the proton-controlled surface reactions.

1. Introduction

Since US EPA posted the solidification/stabilization (S/S) techniques as the best demonstrated available technology (BDAT), cement-based S/S processes have been widely employed for the treatment of hazardous wastes, especially the RCRA regulated metal-bearing wastes [1]. The S/S process is characterized so as to improve the handling and physical characteristics of the wastes by converting them into monolithic forms. The interactions which occur between the wastes and the environment are greatly reduced due to the decrease in waste surface area. Additionally, the

*Corresponding author

solubility and the leaching of the hazardous constituents from the solidified waste matrix into the dynamic environments are appreciably inhibited. Thus, the solidified/stabilized wastes can be safely disposed in landfills so that the contamination of the soil (or groundwater) becomes less possible. The mechanisms where a waste is stabilized by the solidification agents have been previously investigated by several workers and are generalized as (1) chemical bonding between the waste and the agent, (2) physical binding between the waste and the agent, (3) adsorption by the hydration products of the agent, and (4) encapsulation by the solidified matrix [2–4]. Understanding the fixation processes is crucial in predicting the long-term stability and durability of the solidified waste matrix in the environment. However, a controversy still persists regarding whether physical entrapment in the inorganic matrix (micro-encapsulation) or chemical reactions between the waste constituents and the binding materials (chemical interactions) is the principal fixation mechanism or not. Those microchemistry changes have not been easily identified and quantified – even with the aid of sophisticated surface instrumentation [5]. The “binding” natures between the wastes and the solidification agents are fairly difficult to interpret for understanding the stability of the waste forms. Thus, a study on the leaching characteristics becomes an alternative assessment for evaluating the long-term stability of the waste matrix. Methods for evaluating the stability of a solid waste matrix can be generalized as extraction test, batch leach tests and column leach tests [6–8]. In the extraction test, the solid specimen has to be crushed before the test so that the chemical leachability of the waste matrix can be determined. In the leach test, the solid waste matrix is well in contact with the leachant without being crushed. The leachant can be renewed periodically or continuously so that the chemical leachability and physical durability (physical integrity) of the solid matrix can be evaluated. The semi-dynamic or dynamic leaching test is specially favorable for studying the leaching potential and the changes in the physical structure of a waste solid. A complete study on the leaching characteristics of a solidified waste matrix is assumed in this work as being fairly important towards understanding the long-term chemical and physical stability of a matrix. The major cement constituent tricalcium silicate (C_3S) is used here as a model solidification agent for solidifying/stabilizing the copper oxide. The simplified system provides a fundamental basis for obtaining insight into the leaching characteristics of the waste matrix. The interactions between the leaching solution (acetic acid) and the matrix ($C_3S + CuO$) are examined extensively. The time changes of the matrix constituents, physical strength, specific surface area, porosity, and pore size distribution are correlated with the long-term stability and leachability of the solidified/stabilized wastes.

2. Materials and methods

2.1. Materials and sample preparation

All the chemicals used in this work were of reagent grade. Tricalcium silicate (C_3S) was prepared by mixing three moles of calcium carbonate (99.95% purity,

Cerac, Milwaukee, WI) with one mole of fused silica (99.9% purity, Ctist, Taiwan), homogenized with isopropyl alcohol in a ball mill. This was followed by drying at 85 °C environments for 2 h, calcining at 950 °C for two more hours, sintering at 1600 °C for 3 h, and air quenching [9]. The product was ground to pass a #200 sieve for later usage. The C_3S product thus prepared was confirmed by XRD analyses with the data file of the Joint Committee on Powder Diffraction Standards (JCPDS, pattern number 31-301) [10]. Copper oxide (99.9% purity, Gredmann, Taiwan) served as a reference waste in this work. The C_3S product and copper oxide were ground to pass a #325 sieve and a #200 sieve, respectively, for preparing the solidified/stabilized samples. Analytical grade acetic acid (Merck, Darmstadt, Germany) was used in preparing the leachant solutions.

The solidified/stabilized samples of C_3S and copper oxide (4:1 weight ratio) were made by thoroughly mixing them with Milli-Q reagent water (C_3S /water weight ratio 0.5). The newly mixed C_3S /CuO pastes were carefully placed in 1.1 cm (diameter) by 2.2 cm (height) PVC molds. The pastes were allowed to set for 48 h at conditions of 35 °C and 100% humidity before they were removed from the molds and replaced in the same environment for a 28-day curing period. At the end of the curing period, the solidified specimens were used for semi-dynamic leaching experiments and leaching characteristic investigations.

2.2. Methods and analysis

A series of semi-dynamic leach tests on the C_3S /CuO matrix were carried out and 1 N acetic acid was employed as a leachant for simulating the relevant environmental situations. Employing the semi-dynamic leaching process and 1 N acetic acid as leachant made it possible to accelerate the leaching of an index contaminant in this work. Semi-dynamic leaching is a process in which the leachant is renewed periodically after intervals of static leaching. Each experimental run involved leaching a group of specimens. A solution/solid weight ratio of 20:1 was used in the leach tests and the leachant in contact with each specimen was replaced with a new solution on a 24 h basis. The decanted solutions (triplicate specimens) were filtrated through 0.45 μ m filter membrane and saved for pH measurements and Ca, Cu and Si analysis with atomic absorption spectrometry (Perkin Elmer 5000).

The leached specimens were removed from the leachant for subsequent XRD examinations, matrix pH measurement, specific surface area determination, compressive strength test, pore volume and pore size distribution analyses at the predetermined leaching periods. The leached specimens were manually crushed to pass a #200 sieve before XRD examination with the Philips powder X-ray diffractometer (model PW 1729). Operating parameters were: $CuK\alpha$ radiations, 30 kV, and 20 mA. The measured intensities and 2θ values were recorded and analyzed by a computer system. The samples were scanned from 10° to 70° (2θ), and the scanning rate was fixed at 0.05° (2θ) per second. Matrix pH measurement followed that of Method of Soil Analysis [11]. The leached specimen was first dried in an oven at 50 °C for 5 h and was ground to pass a #200 sieve. Thereafter, the treated sample powder was mixed with 0.01 M $CaCl_2$ (liquid and solid ratio of 2 ml versus 1 g), and the mixture was

subject to shaking for 24 h before the pH measurement. For a specific surface area, pore volume and pore size distribution measurements, the leached specimens were dried in an oven at 105 °C before the measurements with an automatic physisorption analyzer (Micromeritics ASAP 2000) using N₂ and He carrier gases. The sensitivity of the Micromeritics analyzer covers pore sizes from 0.002 to 0.2 μm. For larger pores exceeding this detection limit, the mercury porosimetry was employed with Micromeritics Autopre II 9220 for pore sizes up to 292.4 μm. Solid physical strength measurement was carried out with a material test system (MTS High Rate Test System Model 819-10S). The rate of load increase was fixed at 0.5 mm/min.

3. Results and discussion

Leaching is a process in which the contaminants confined in the solid phase are transferred to the leachant in contact with it through various pathways. The CuO solidified with C₃S pastes is vulnerable to the acid attack. Thus, the leaching of copper from the C₃S/CuO matrix in an acetic acid solution is to be expected. Figure 1 shows

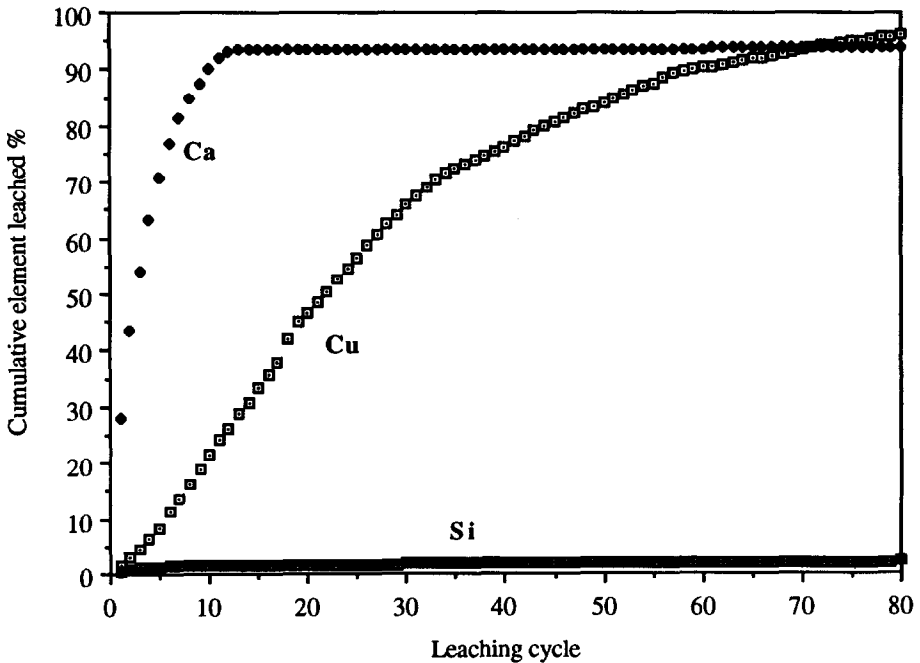


Fig. 1. Cumulative percentage of Ca, Cu, and Si leached out of the C₃S/CuO solid matrix using semi-dynamic leaching procedures. Total Ca, Cu, and Si in the solid matrix are 1.613, 0.691, and 0.395 g, respectively.

the cumulative release of Cu, Ca and Si from the C_3S/CuO matrix under the degradation of 1 N acetic acid solution. The release of Ca is both rapid and complete, as indicated from this figure. In about 10 extractions, the amount of Ca that is released reaches the maximum, which is about 90% of the total Ca in the system. The release of Cu constantly increases in the initial 30 extractions, corresponding to 66% of the total Cu solidified. On the contrary, the leaching of Si was very insignificant; only 2.0% of the total Si was transferred to the solution in 80 extractions. For comparison, a system containing CuO only or SiO_2/CuO was also subject to the leaching by acetic acid. The cumulative copper released as a function of the leaching cycle is presented in Fig. 2. Under identical leaching conditions, a system with only CuO would release much more dissolved copper to the solution than the SiO_2/CuO and C_3S/CuO systems. The release of Cu is clearly indicated from the results as being closely related to the release of Ca and the exposure of CuO to the leachant in the matrix.

XRD is an excellent tool for studying the morphological changes and appearance or disappearance of different phases. A previous study on the reaction mechanism of C_3S has shown that the major products of the C_3S hydration reaction are unhydrated C_3S , $CaCO_3$, $Ca(OH)_2$, and calcium silicate hydrate ($1.5CaO-SiO_2-xH_2O$, CSH) [10]. The qualitative XRD patterns for the C_3S/CuO solidified matrix are shown in

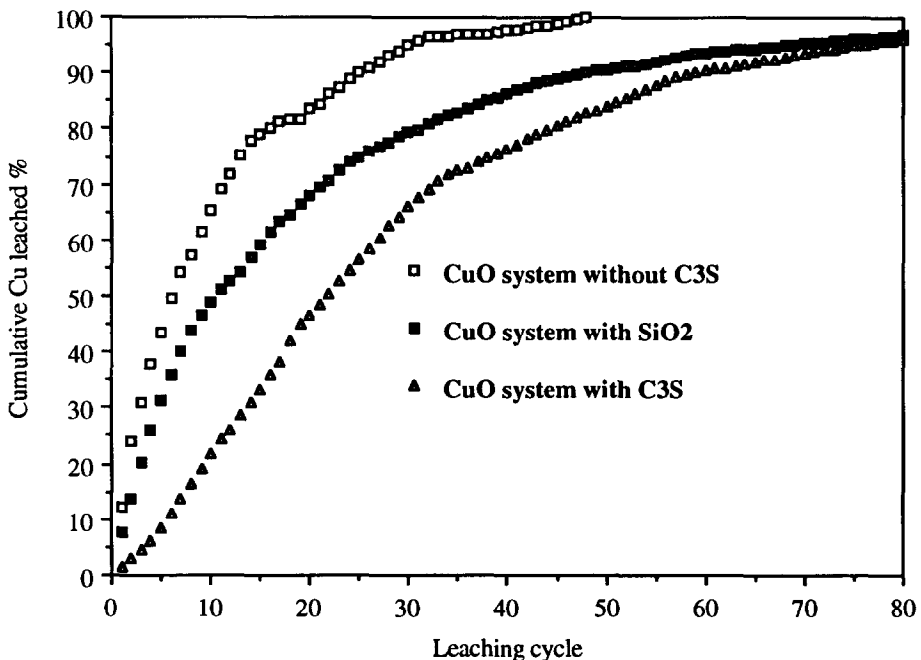


Fig. 2. Cumulative percentage of Cu leached out of the CuO only, SiO_2/CuO , and C_3S/CuO solid matrix systems using semi-dynamic leaching procedures.

Fig. 3a. Figure 3a indicates the presence of CuO, unhydrated C_3S , $CaCO_3$, $Ca(OH)_2$, and calcium silicate hydrate ($1.5CaO-SiO_2-xH_2O$, CSH). The presence of $Ca(OH)_2$ and $CaCO_3$ would certainly indicate an alkaline environment in the C_3S matrix system. The disappearances of copper and the major constituents of C_3S pastes were

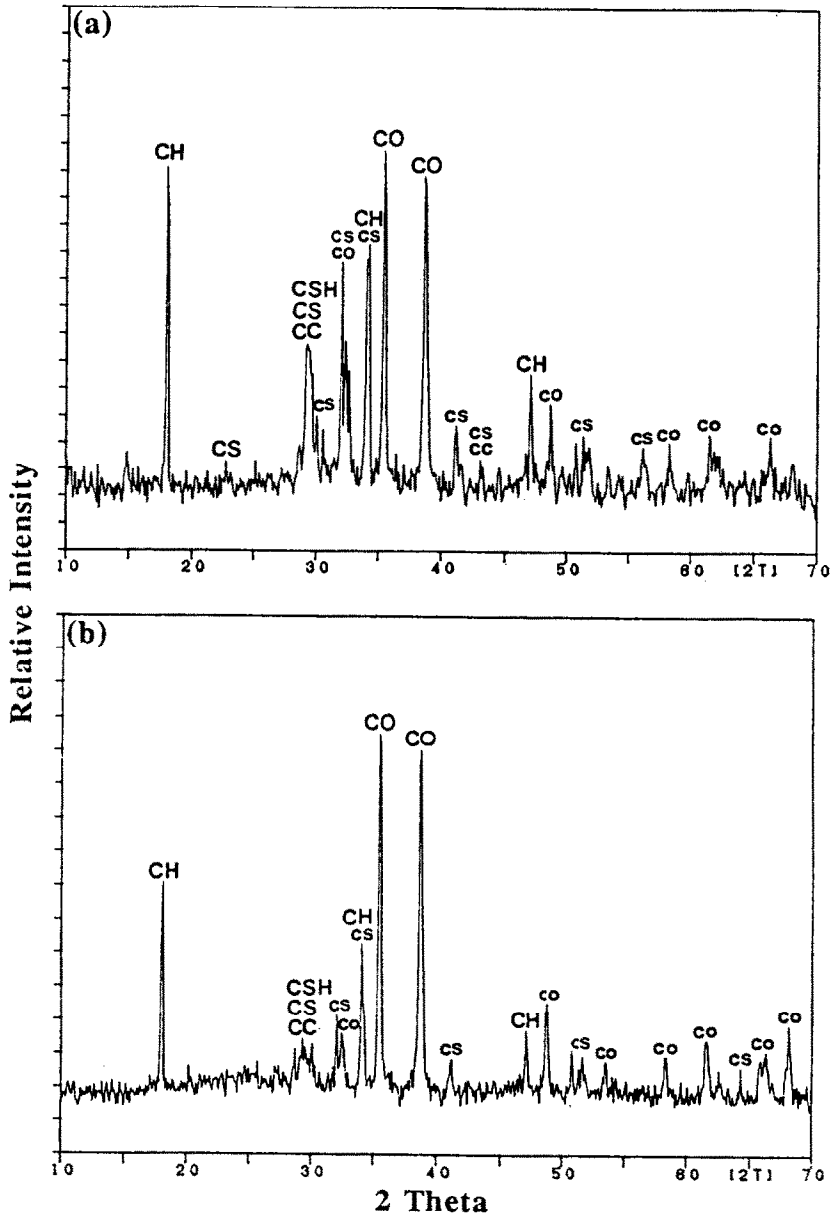


Fig. 3a-b.

examined via XRD. Figure 3b–3f presents the XRD patterns of the leached C_3S/CuO systems at 3, 7, 10, 28, and 80 days, respectively. After three extractions (Fig. 3b), a decrease was found to occur in the relative crystal intensities of $Ca(OH)_2$, $CaCO_3$, unhydrated C_3S , and CSH. After seven extractions, only significant CuO and trace

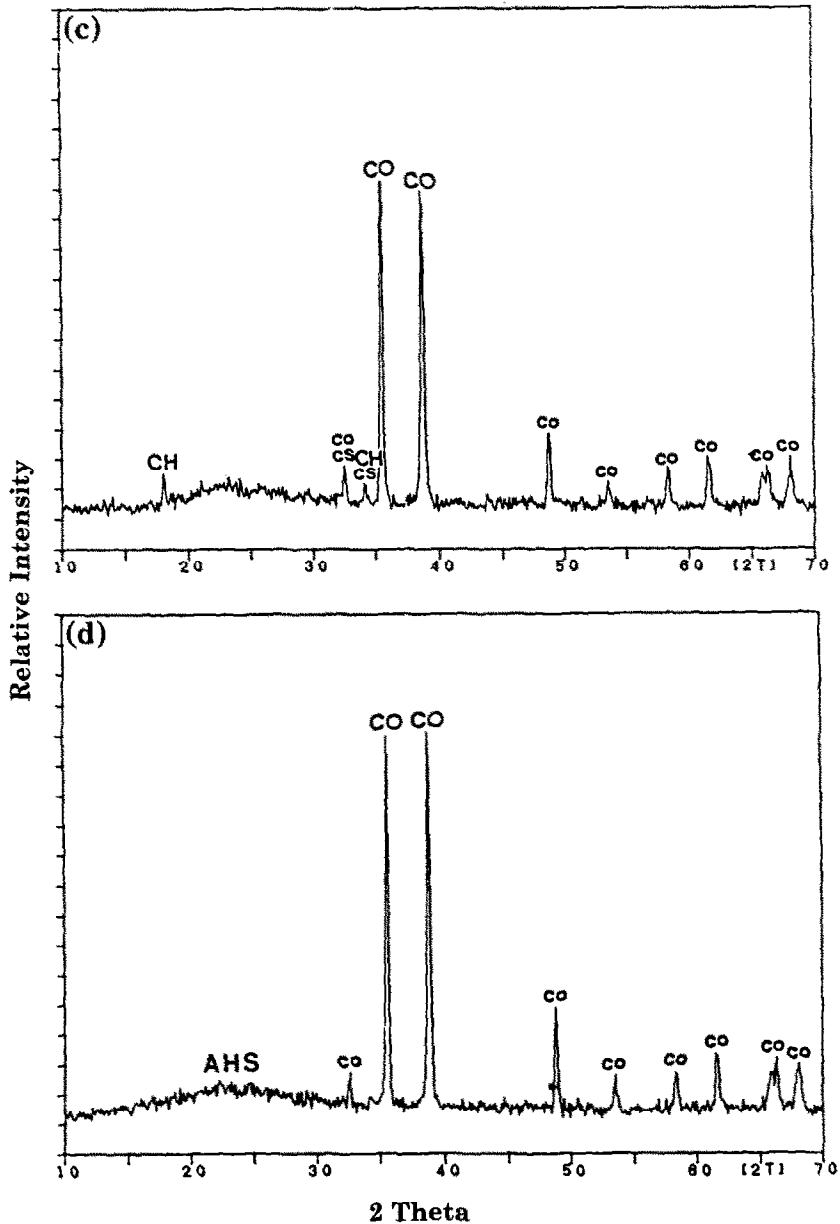


Fig. 3c-d.

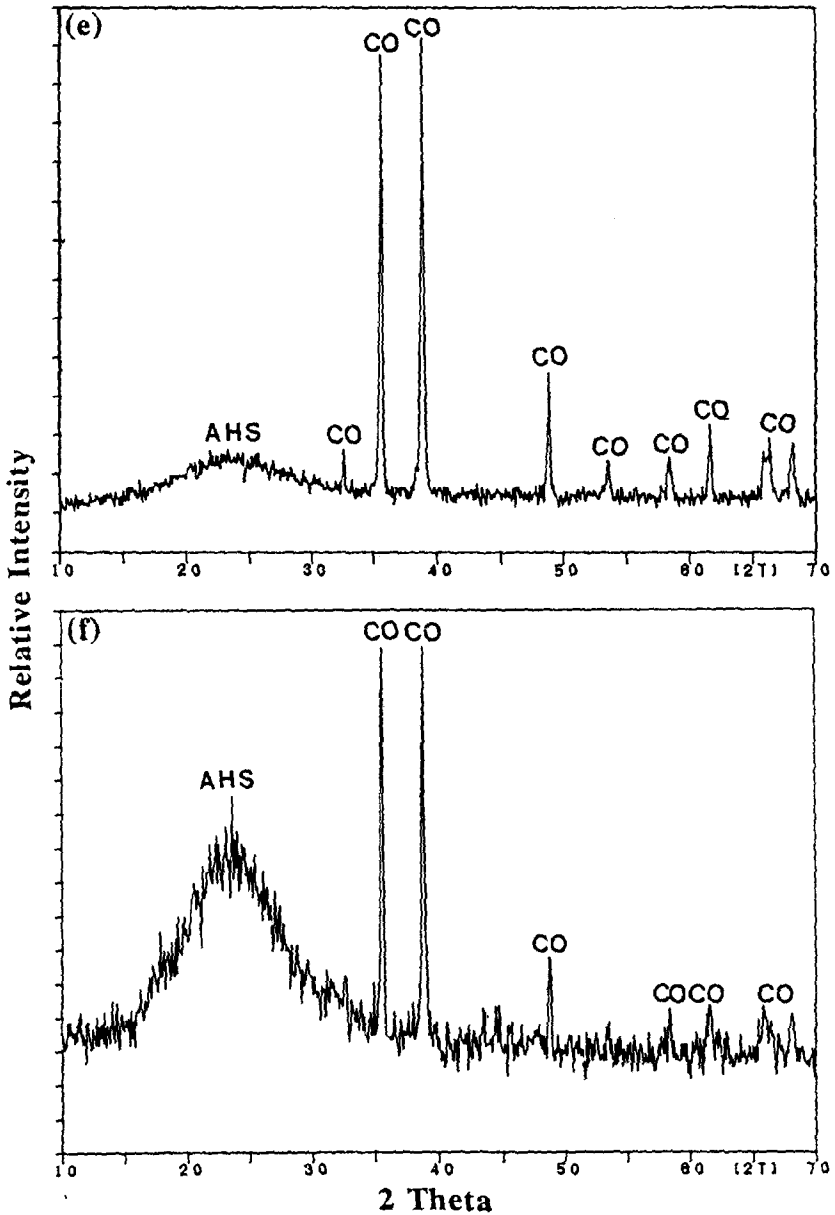


Fig. 3. XRD patterns of the C_3S/CuO solid matrix: (a) unleached matrix; (b) after three extractions; (c) after seven extractions; (d) after 10 extractions; (e) after 28 extractions; (f) after 80 extractions. Symbols are as follows: CC, calcium carbonate ($CaCO_3$); CH, calcium hydroxide ($Ca(OH)_2$); CO, copper oxide (CuO); CS, tricalcium silicate ($3CaO-SiO_2$); CSH, calcium silicate hydrate ($1.5CaO-SiO_2-xH_2O$); AHS, amorphous hydrated silica.

$\text{Ca}(\text{OH})_2$ crystal peaks were detectable. It is important to notice that the formation of amorphous hydrated silica is emerging. After 10 extractions, no crystal peaks of C_3S hydration products were undetectable. However, amorphous hydrated silica has appreciably increased. Only amorphous hydrate silicate and CuO were identified in the XRD patterns of the leached $\text{C}_3\text{S}/\text{CuO}$ solidified matrix at 28 and 80 extractions, respectively. These patterns are quite similar except for the relative peak intensities of CuO and amorphous hydrate silica. The increase in the relative intensity of amorphous hydrate silicate might possibly imply the increase in the relative amount of silica compounds in the leached residual.

The pore volume and pore size distribution of the unleached $\text{C}_3\text{S}/\text{CuO}$ matrix are presented in Fig. 4a. Most of the pore volumes of the $\text{C}_3\text{S}/\text{CuO}$ forms are quite evidently contributed by pores with diameters of $0.7\text{--}2\ \mu\text{m}$. These results are quite consistent with the reported capillary pore sizes ($0.01\text{--}10\ \mu\text{m}$) of the cement pastes and cement-based waste forms [8]. The major pore sizes are distributed over the range $1\text{--}10\ \mu\text{m}$, as indicated from an examination of the pore size distribution after leaching

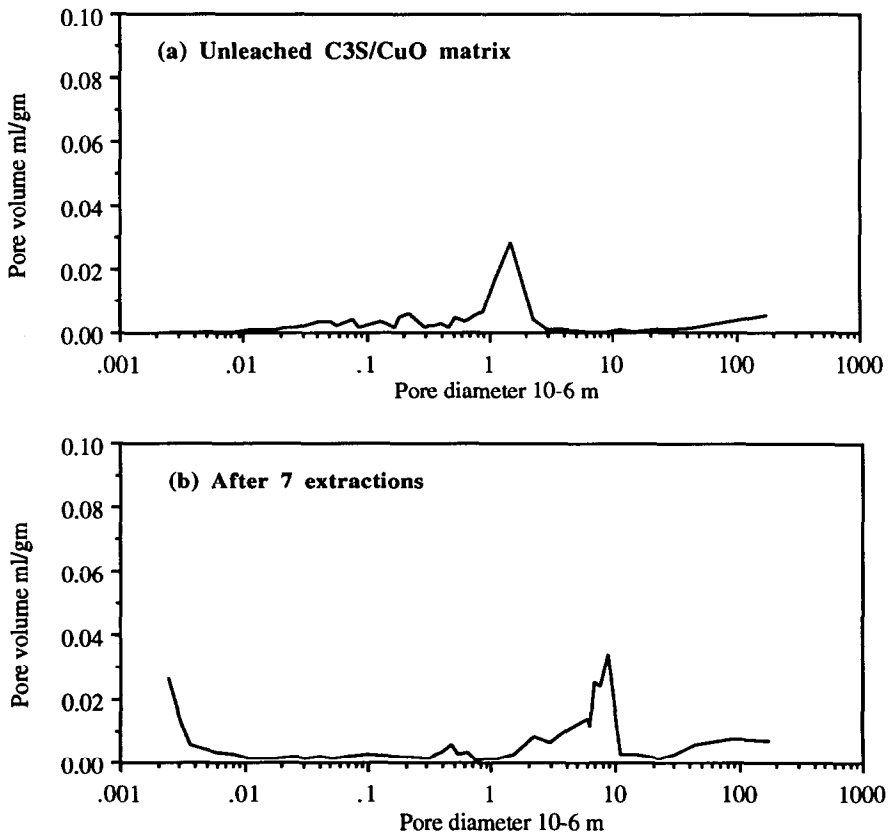


Fig. 4a-b.

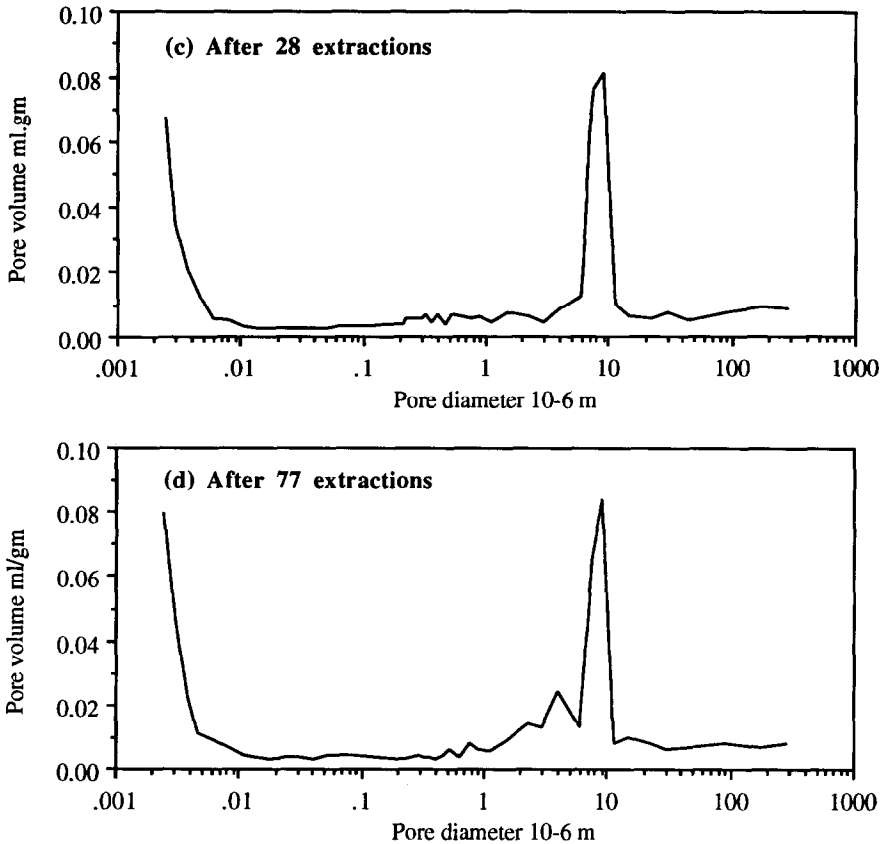


Fig. 4. Pore volumes of the C_3S/CuO solid matrix as a function of the pore size distribution.

(Fig. 4b-4d). However, the pore volume contributed by these pores has increased appreciably. The significant changes in the small pores ($0.001-0.1 \mu m$) were also confirmed by a comparison of Fig. 4a with Fig. 4b-4d.

The changes of specific surface area and the pore volume of the leached matrix are presented in Fig. 5. Both BET specific surface area and pore volume of the leached C_3S/CuO solidified matrix have a dramatic increase in the first 20 extractions. The specific surface area increased to nearly $440 m^2/g$ at 20 extractions and pore volume increased from $0.02 ml/gm$ of the unleached matrix to $0.25 ml/gm$ on 14 extractions. The increase in the BET specific surface area of the leached matrix can be attributed to the increase of the smaller pores. The generation of smaller pores and the enlargement of the original pores due to the leaching of the matrix constituents may possibly result in both an increase in the transport of solutes and an enhancement in the interfacial reactions between the leachant and the matrix compounds.

The influence of leachant on the physical strength of the C_3S/CuO solid matrix is shown in Fig. 6. The compressive strength of the unleached C_3S/CuO solid is as high

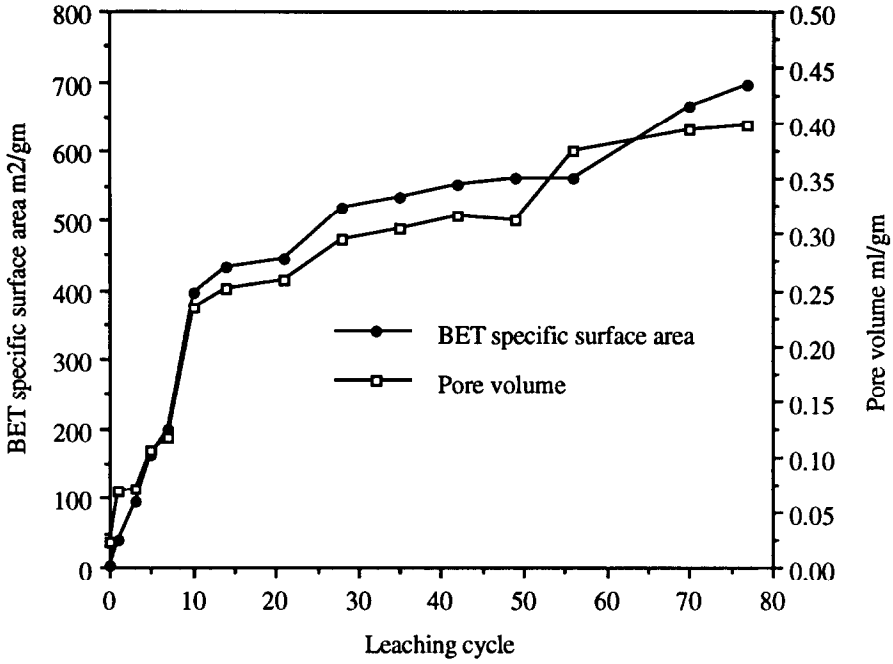


Fig. 5. Changes in BET specific surface area and pore volumes of the leached C₃S/CuO solid matrix.

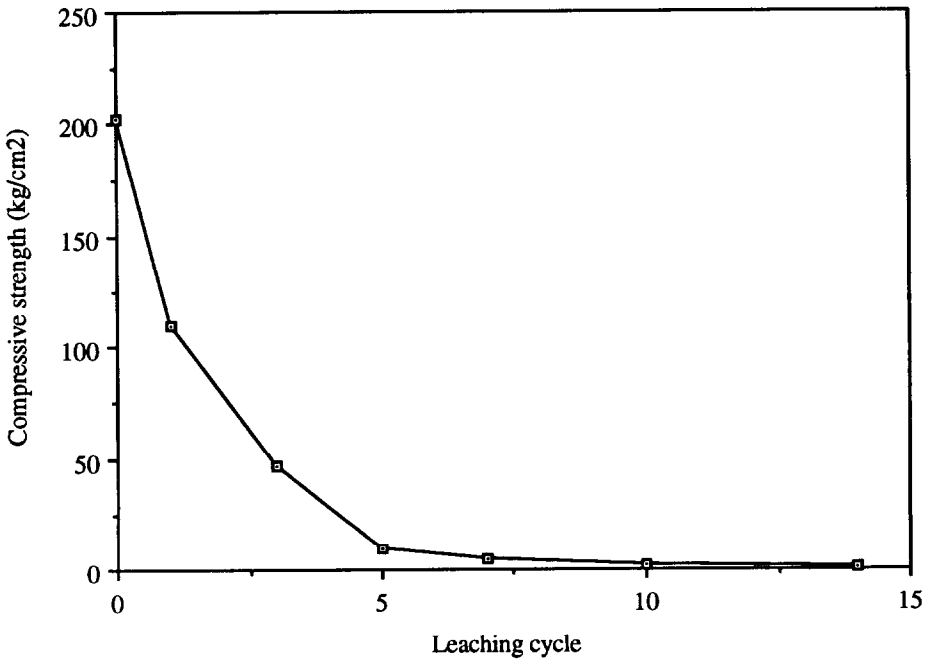


Fig. 6. Changes in physical strength of the unleached and leached C₃S/CuO solid matrix.

as 202.5 kg/cm². However, the compressive strength is only 4.7 kg/cm² and 0.6 kg/cm² after 7 and 14 extractions, respectively. The dramatic decreases in the physical strength of the solid matrix can be accounted for by examining the dissolution of Ca, the changes in XRD patterns, the increases in pore volume and pore size. Principally, the loss of physical strength is due to the extraction of calcium gel. This loss certainly causes the left Si-rich skeleton to have almost no physical strength.

The immobilizing mechanisms of the C₃S system can be generalized as: chemical bonding or physical binding between waste and agent, adsorption, precipitates encapsulated by the intact solid matrix, and confinement of the dissolved contaminants in pore water. A carefully solidified/stabilized waste would have the capability of either immobilizing the contaminants in the matrix or else limiting the leaching potential of the hazardous materials. The molecular diffusion is fairly unlikely to occur even with the maximum concentration gradient of the indexed constituents across the boundary of the solid matrix and the leaching solution because the permeability of the cement-based matrix is as low as 10⁻⁵–10⁻⁹ cm/s [12]. The leaching of cement-based waste forms, with water being incapable of causing any noticeable “damage” on the waste forms, has been previously reported in several studies [13, 14]. Nevertheless, leaching becomes quite evident when acidic solution is acting on the solid matrix. System pH should be a controlling factor affecting the leaching characteristics of the waste solid forms [15]. Via the model C₃S/CuO system, the hydration products of Ca(OH)₂ and CaCO₃, which provide alkalinity to neutralize the acids, have been demonstrated in this work to dissolve very rapidly (Fig. 1). The dissolution of calcium compounds would catalyze both the disintegration of the waste matrix and also the loss of the physical strength. The dissolution of minerals has been extensively studied [16–19]. Stumm et al. proposed that the proton-promoted surface reaction is the mechanism for most of the dissolution processes in nature [16–18]. It is believed that the dissolution of calcium is primarily due to the proton-promoted surface reaction in the matrix, along with the rate of dissolution being closely related to the activity of proton at the solid/water interface. As the dissolution reaction proceeds, the unhydrated C₃S would come in contact with water so as to undergo a hydration reaction which would subsequently form the calcium compounds and calcium silicate hydrate. Meanwhile dissolution of calcium compounds is forced to continue as the leachant has been periodically renewed so as to maintain the system at low pH conditions. This phenomenon is shown in Fig. 7, in which the system pH drops from 4.1 to 2.3 after 17 extractions, and the matrix pH drops from 12.5 to 4.3 after 20 extractions. The decreases in system and matrix pHs, along with the dissolution of calcium compounds, would leave larger, or produce new, voids in the solid. Consequently, the leaching process would be enhanced by increasing the metal solubility and solute mobility (the permeability is increased). The rate of solute transport is greatly accelerated because increases in specific surface area and pore volume (Figs. 4 and 5) provide additional reacting sites for the matrix compounds and waste constituents to dissolve.

Most of the silica compounds do not dissolve during the semi-dynamic leaching tests (Fig. 1). At the final stage of leaching, 96% of the total copper, 94% of the total calcium, and 2% of the silica were leached out from the solid matrix into the acetic

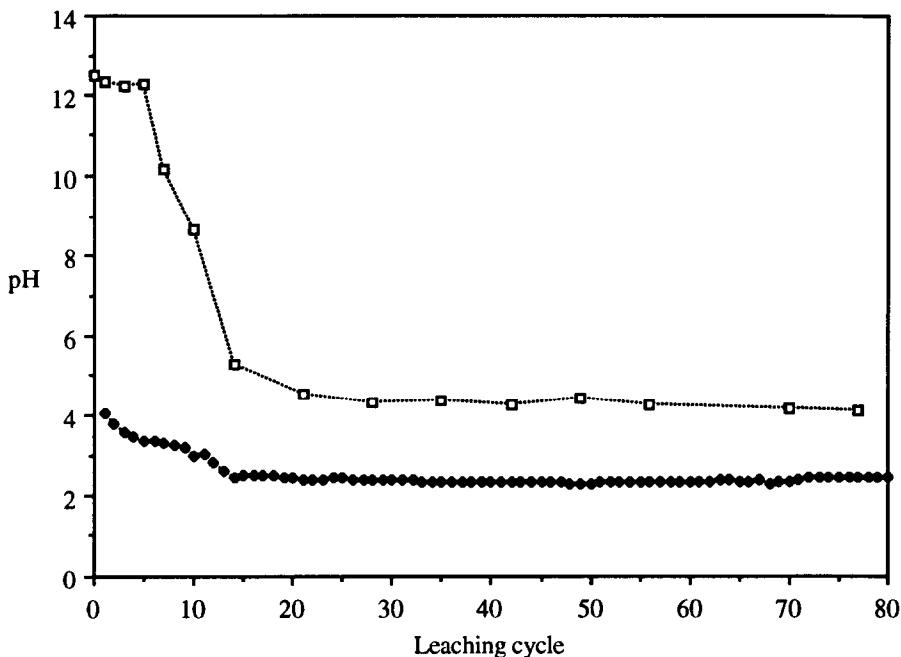


Fig. 7. Variation in the pH of the powdered C_3S/CuO matrix and the leachant under dynamic leaching conditions. (□) pH of the powdered matrix; (◆) pH of the leachant.

acid solution. The residual skeleton of the leached waste matrix would be a silica-rich structure (amorphous hydrate silicate, Fig. 3) and certainly bears little physical strength. However, these silica-rich disintegrated structures still play a role in immobilizing the copper – even after the calcium compounds are completely depleted. Adsorption of copper on silica compounds and the micro-encapsulation of CuO by silica compounds as depicted in Fig. 2 must be the controlling mechanism at this stage.

4. Conclusions

Immobilization of the hazardous constituents in the solid matrix can be attributed to the chemical or physical binding between the waste and the solidification agent, the adsorption of the hazardous ions on the solidified compounds, and physical encapsulation. Micro-entrapment is the principal fixation mechanism which confines the hazardous materials from leaching. The low permeability of the solid wastes makes the diffusion of the hazardous solutes fairly unlikely to cross the boundary of leachant and solid surface. The dissolution of calcium compounds is observed in this present work as being critical to the failure of the fixation ability of the solid matrix and the

leaching of solidified hazardous materials. Dissolution of calcium compounds in the matrix would increase the number of pores and pore size and therefore enhance the dissolution reactions and solute transport within the matrix. Dissolution of the hydration products has been promoted by the proton-controlled surface reactions. Silica compounds might play a role in the adsorption and micro-entrapment of copper at the final stage of the leaching. The acid-resistant materials are apparently necessary for rendering the solidified waste matrix to maintain its physical integrity and strength, thereby providing long-term stability.

Acknowledgments

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