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Mineralogical alterations that affect the durability and metals containment of aged solidified and stabilized wastes

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Abstract

Detailed research on the weathering and degradation of solidified and stabilized wastes once treated materials have been buried is lacking, and published data to verify the long-term performance and durability of landfilled treated wastes over time are still only limited. Optical and electron microscopy techniques were used in this study to evaluate features associated with metal-bearing contaminated soil and industrial wastes that have been solidified and stabilized with Portland cement and stored outdoors, archived in the laboratory, or buried on site. Results show that although the extent of degradation after 6 years is considered slight to moderate, the same environmental factors that affect the durability of concrete also must be considered when evaluating the durability and permanence of cement-stabilized and solidified wastes. Furthermore, evaluations of durability and permanence cannot be based on leaching and chemistry analyses alone. The use of all levels of microscopic analyses are needed to accurately evaluate the long-term performance of solidification/stabilization technologies. In addition, regulations for the on-site burial of treated wastes, even after they are rendered nonhazardous, are needed. Burial of cement-based solidified and stabilized wastes in deleterious environmental zones, such as acid or saline soil, as well as fluctuating groundwater systems is not recommended.

Keywords: Microstructure; Degradation; Durability; Heavy metals; Waste management

1. Introduction

Most research conducted on solidified and stabilized wastes has been acquired through chemical, physical, and leaching tests on treated wastes, typically collected during treatability studies, technology demonstrations, or from wastes that have been synthesized in the laboratory. Despite the increased use of solidification/stabilization (S/S) remediation technologies for soils, sludges, and industrial wastes prior to disposal in landfills or directly on site, little published data are available to verify the durability and permanence of such landfilled wastes over time [1]. Evaluations of durability commonly rely on the American Society for Testing and Materials (ASTM) standardized wet/dry and freeze/thaw cycling tests, as well as unconfined compressive strength tests [2,3]. However, the resistance of concrete to attack by chemical or physical agents is not necessarily related to its mechanical strength. It does not follow that because a concrete material has ample strength to fulfill the purpose for which it was designed, it will resist attack and disintegration in any environment in which it is placed [4].

In addition, bulk chemistry and leaching tests, such as the U.S. Environmental Protection Agency's (EPA) Toxicity Characteristic Leaching Procedure (TCLP), frequently are used to evaluate long-term S/S treatment effectiveness [5–7]. Such destructive analyses do not consider the mineralogical phases and microstructure of the treated waste materials being tested. Reports of failed solidified wastes suggest that unsuitable inorganic materials have been used widely without regard for long-term properties and field performance; however, there is still a lack of fundamental field data related to the long-term performance of solidified and stabilized products following their disposal [8,9].

Physical and chemical weathering and the deterioration of solidified and stabilized wastes are complex processes that can be determined best by in situ microscale analyses of the chemical and physical stability of mineral phases present in the treated material [10,11]. In this study, optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), as well as electron probe microanalyses (EPMA), were used to evaluate the permanence of metals containment in several solidified

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and stabilized wastes that had been landfilled or stored above ground as long as 6 years.

2. Experimental methods

Sample cores of seven solidified and stabilized waste types that were either archived in the laboratory, stored outdoors, or landfilled on site for up to 6 years were obtained from several EPA sources, including the Superfund Innovative Evaluation Technology (SITE) demonstration program. Sampling procedures and characteristics of the individual waste types under investigation have been documented in previous studies [2,6,12]. Those studies also provide physical, chemical, and leaching test data for the treated wastes, as well as documentation of sample preparation techniques. In addition, bulk X-ray diffraction analyses are described [12]. Details specific to the microscopy analyses are presented below.

2.1. Petrographic analyses

Opaque materials, such as the metallic waste contaminants, were evaluated using reflected light microscopy, while plane and polarized transmitted light was used to observe transparent and translucent concrete components of the treated waste samples and to evaluate the micromorphic relationship between the cement paste and the constituents of the hazardous waste. In addition, ultraviolet (UV) reflected light was used to determine porosity and to evaluate the nature of voids within the treated waste samples. Small blocks of the solidified and stabilized wastes were impregnated with epoxy containing a UV-fluorescent dye. Thin sections were prepared by a professional petrographic laboratory using standard cement and concrete sample preparation techniques. The same thin sections also were used for the SEM and EPMA.

2.2. SEM

Epoxy-impregnated, highly polished thin sections of the treated waste samples were analyzed using a JEOL (Model 840, JEOL Inc., Akashima, Japan) scanning electron microscope equipped with a LaB_6 filament and an energy dispersive X-ray (EDX) spectrometer. Backscattered electron (BSE) images were used primarily to differentiate metal contaminants having atomic numbers higher than that of the surrounding cement matrix. EDX microanalyses provided nondestructive, qualitative chemical compositions of the cryptocrystalline and amorphous cement paste, as well as the metal contaminants contained in the cement admixtures. Elemental distribution maps were used to provide detailed information on chemical zoning and textural relationships that were not always apparent from BSE images or optical photomicrographs.

2.3. TEM

Electron diffraction patterns of selected metal contaminants and cement constituents were obtained using a JEOL (Model JEM-2010) transmission electron microscope equipped with EDX spectrometry capabilities. Chemical compositions obtained by EDX spectrometry aided in the identification of metal-bearing minerals through the use of selected area diffraction spot or ring patterns.

2.4. EPMA

Treated waste samples containing metals with overlapping characteristic X-ray energy peak spectra, including arsenic (K-alpha) and lead (L-alpha), arsenic (L-alpha) and magnesium (K-beta), sulfur (K-alpha) and lead (M-alpha), barium (L-alpha) and titanium (K-alpha), and phosphorus (K-alpha) and zirconium (L-alpha) were chemically analyzed using a JEOL (Model 8900) electron probe equipped with wave-length dispersive X-ray (WDX) spectrometry capability. Those combinations of elements cannot be resolved by EDX spectrometry alone. The spatial distribution of specific elements was recorded as two-dimensional elemental maps, thus providing reliable representations of the distribution of the elements under investigation.

3. Results and discussion

Field macro-, micro-, and submicroscopic analyses were used to evaluate physical and chemical alterations of the treated waste monoliths. These analyses provided evidence of movement of metals and other mineral constituents in solidified and stabilized wastes stored under varying environmental conditions.

3.1. Physical alteration

Field observations of monoliths of solidified and stabilized wastes that were stored outdoors showed abundant cracking. Macrovoids within such monoliths consisted predominantly of planar voids as much as 1 m in length and 1–5 mm in width. In addition, vesicles as large as 6 mm in diameter were observed. The planar voids commonly show characteristic “Isle-of-Man” or pattern cracking, also known

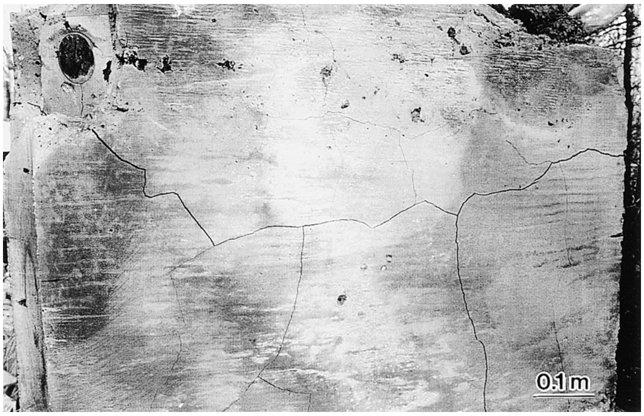

Fig. 1. Typical crack pattern in monoliths of treated waste stored outdoors and above ground.

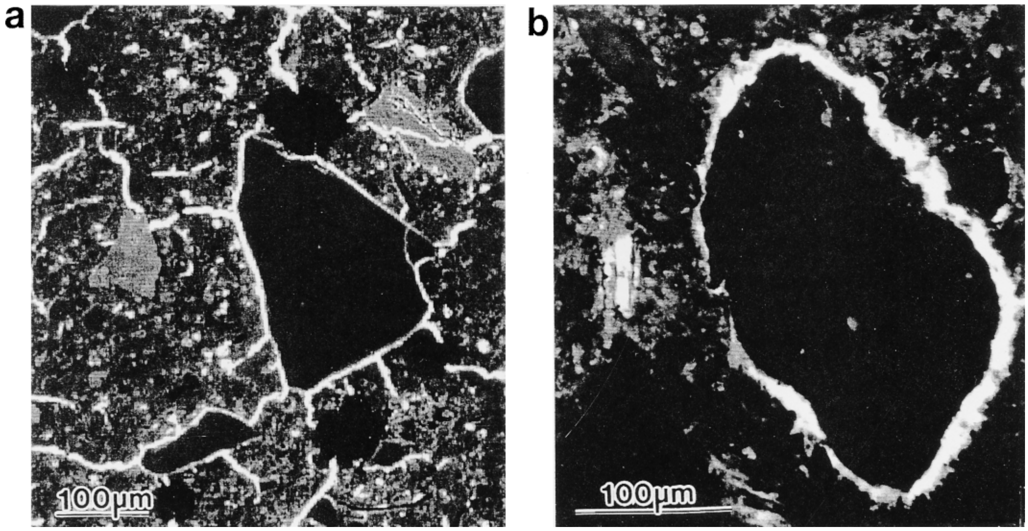

Fig. 2. (a) SEM image and (b) optical photomicrograph under UV fluorescent light of typical microcracks.

as map cracking or crow's-foot cracking (Fig. 1). It is recognized that such patterns indicate expansion cracking in concrete, including plastic shrinkage cracking, as well as expansion resulting from chemical reactions within the concrete [13]. Macroscopic vertical cracks observed in the monoliths of treated waste are characteristic of freeze-thaw action. Other treated waste materials included macrovoids that consisted of irregular cavities as large as 3 cm in length and 1 cm in width. Such irregular voids represent incomplete compaction of air space created during the pouring of semisolid cement admixtures into frames that initially give form to the monoliths.

Within the monoliths of treated waste, microscopic and submicroscopic cracks occur ubiquitously within the cement paste itself, or in association with aggregates of cement and waste (Figs. 2 and 3). Cracks commonly are unfilled; however, some cracks are filled or lined with silica gel, ettringite, or microcrystalline calcite. Cracking in concrete may be caused by a number of factors, including insufficient air-void content, drying and plastic shrinkage, chemical reactions that cause expansion, and freeze-thaw action.

3.2. Chemical alteration

Chemical alteration of the cement paste was observed in all of the treated wastes. Carbonate material precipitated around pockets of unmixed waste material and along the lower portions of some vertical cracks was prominent at the macroscale (Fig. 4). Microcrystalline precipitates of calcite within the cement paste also were observed in direct associ-

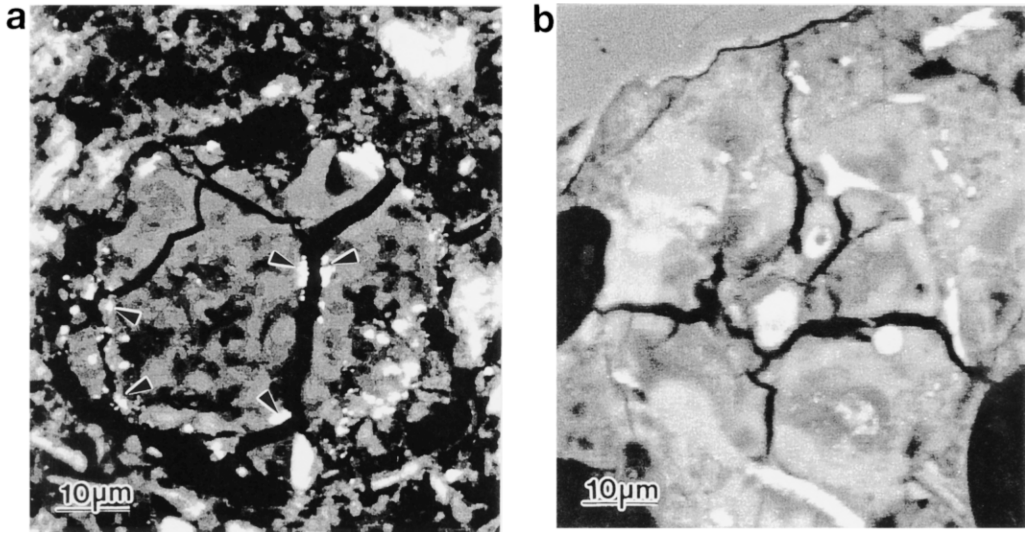

Fig. 3. BSE images of microcracks within a waste aggregate containing (a) lead contaminants (shown by arrows) and (b) cement paste.

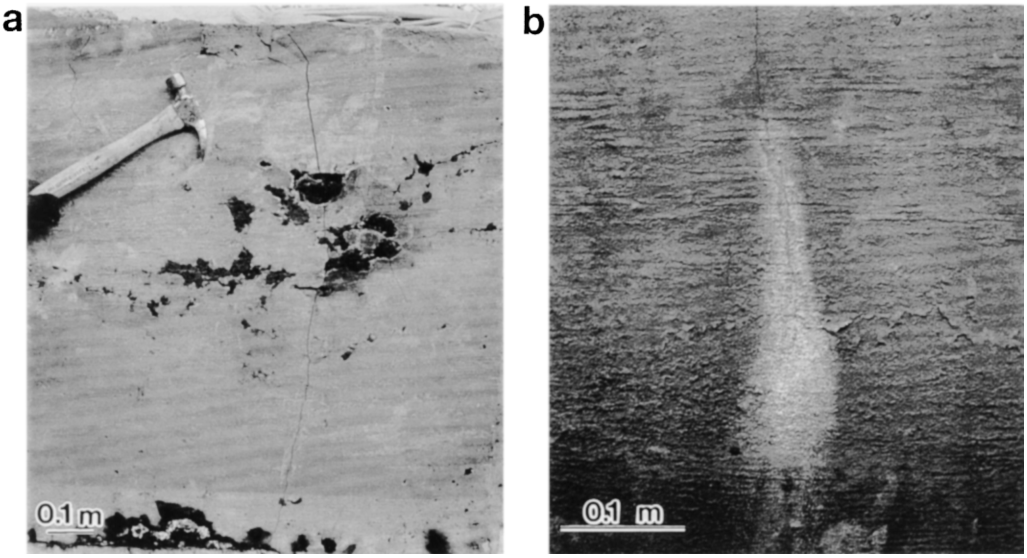

Fig. 4. Carbonate alteration (a) around pockets of unmixed waste and (b) along vertical fractures.

ation with macro- and microfractures, as well as with packing voids. Such features typically are associated with carbonation, a form of carbonate alteration, as well as alkali-silica reactions in concretes where macroscale leaching deposits of calcium carbonate along vertical fractures are common [13].

Cracking caused by secondary chemical reactions is commonly the result of the formation of expansive minerals, such as ettringite, thaumasite, monosulfate, gypsum, and alkali silica gel, intergrown within the hardened cement paste in which crystal expansion is not accommodated and therefore destructive to the concrete structure [14]. Amorphous to cryptocrystalline ettringite and thaumasite were identified within the cement paste through the use of TEM, selected area electron diffraction patterns, and EDX spectroscopy signatures, as shown in Figs. 5 and 6. Alkali-silica gel and microcrystalline gypsum also were observed frequently within the cement paste.

Movement of metals from waste aggregates into the surrounding cement paste commonly was observed through the use of both optical and electron microscopy. For example, migration of lead from dense, opaque waste aggregates into the surrounding cement paste was observed under optical and SEM as alteration zones around cores of metallic lead [Figs. 7(a) and (b)]. Associated TEM selected area diffraction patterns and EDX spectra verify the presence of cryptocrystalline lead aluminum oxide and amorphous lead oxide intercalated within the cement paste [Figs. 8 (a) and (b)]. Amorphous to cryptocrystalline masses of the cement mineral alite also were observed containing lead [12]. Lead (II)

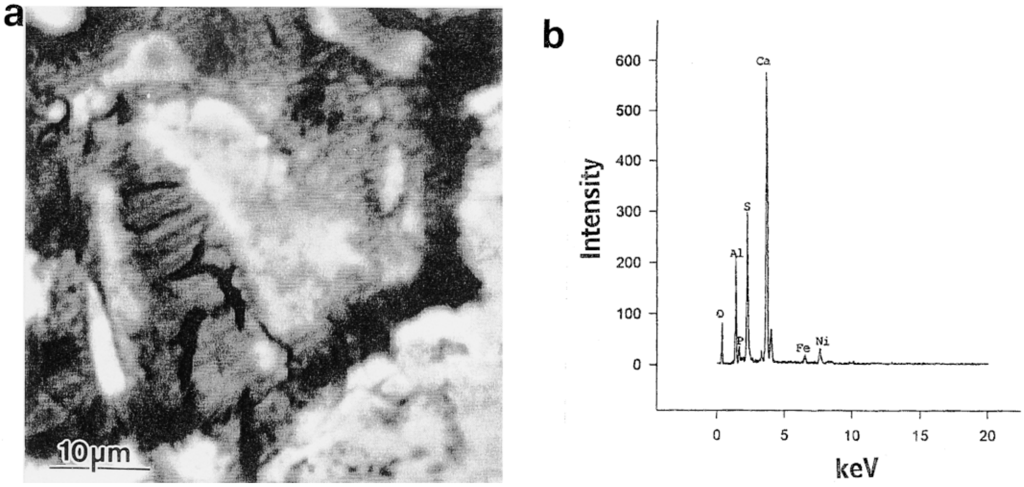

Fig. 5. (a) SEM image of microcrystalline ettringite with (b) characteristic EDX spectra.

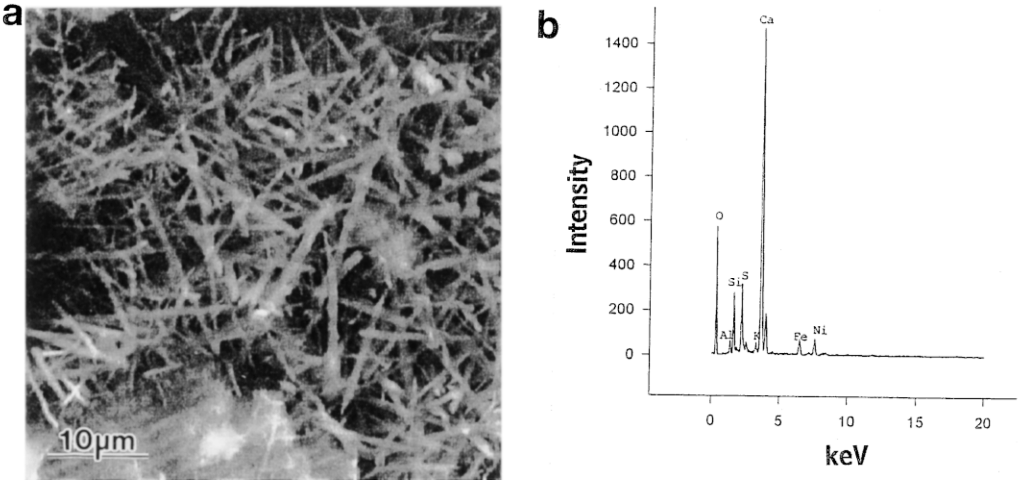

Fig. 6. (a) SEM image of microcrystalline thaumasite with (b) characteristic EDX spectra.

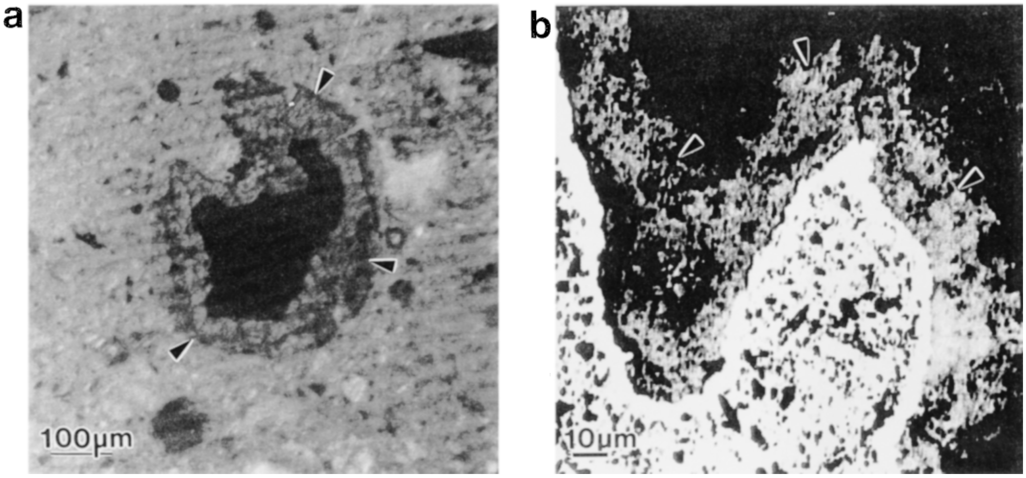

Fig. 7. (a) Photomicrograph and (b) BSE image of metallic lead waste aggregate with alteration zones (shown by arrows).

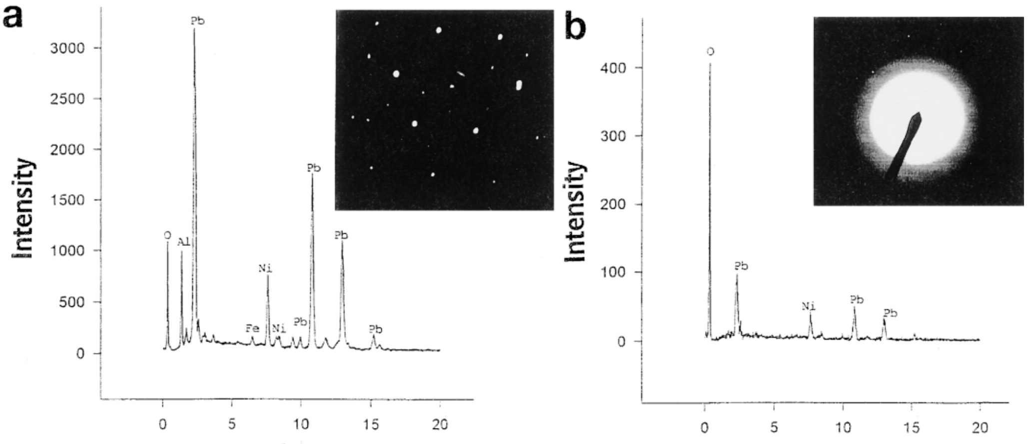

Fig. 8. TEM selected area diffraction patterns and EDX spectra of (a) cryptocrystalline and (b) amorphous alteration zones.

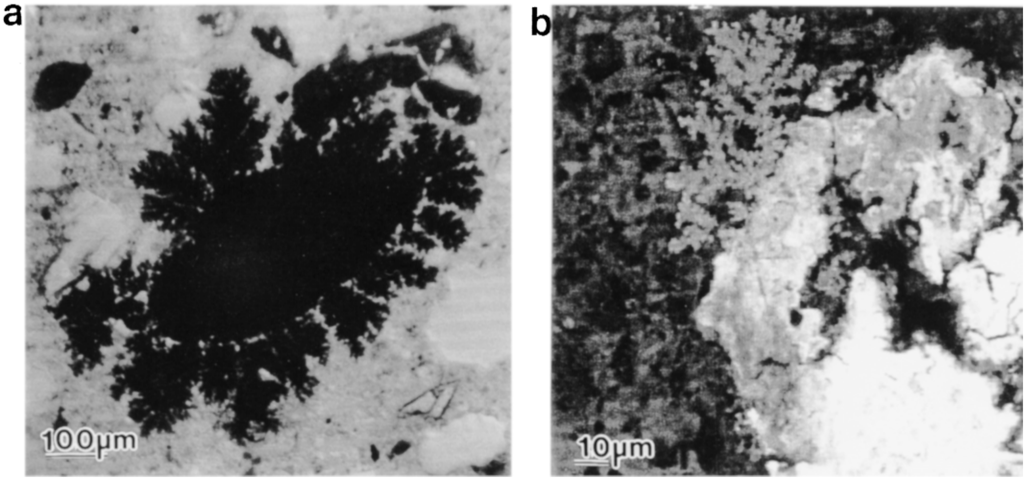

Fig. 9. (a) Photomicrograph and (b) BSE image of copper dendrites on waste aggregates.

cations may have (1) diffused away from the waste aggregate and substituted for calcium in the cement hydrates; (2) precipitated as oxides within the micropores; or (3) been adsorbed onto the amorphous cement paste.

Zinc commonly was observed to be disseminated throughout the cement paste as halos around metallic waste fragments that contain zinc and other metals, such as aluminum, copper, and nickel. As was common with the lead contaminants, such halos, observed on microprobe wave-length dispersive X-ray (WDX) elemental maps, were not recognizable when the same opaque fragments were viewed under visible or reflected light [12]. The lack of apparent alteration of the cement paste as seen in the thin sections suggests that zinc cations also may have diffused from the original metal contaminant and may have been adsorbed to the surrounding cement paste.

Migration of copper also was observed in samples of solidified and stabilized waste that contained copper-rich wastes aggregates encapsulated in the cement paste. Various stages of dendritic overgrowths were observed over a 2-year period, as shown in Fig. 9. As a result of exposure to fluctuating humidity conditions (as high as 90%), hydration of copper-rich waste aggregates formed the hydrated copper sulfate mineral chalcanthite. BSE imaging and EDX elemental mapping show movement of copper without the associated sulfur into a crack within the calcium and copper-rich waste aggregate (Fig. 10).

3.3. Implications for the durability of landfilled solidified and stabilized wastes

Currently, EPA's regulatory criterion for toxicity characteristic requires use of the TCLP to determine if a waste is hazardous [15]. In addition, EPA also requires use of the paint filter liquids test (PFLT) to determine if free liquids

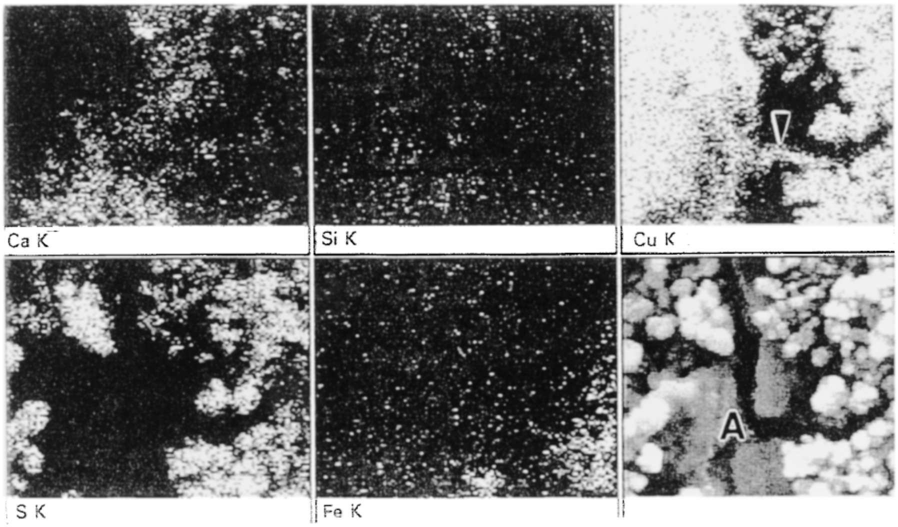

Fig. 10. EDX elemental maps and BSE image of hydrated copper sulfate (chalcanthite) formed on and within crack (shown by arrow) of waste aggregate (A).

are present in a waste before it is disposed of in a hazardous waste landfill. Neither the toxicity characteristic nor the requirement prohibiting placement of liquid wastes in landfills, along with their respective tests, however, is adequate for determining the durability or permanence of metals containment of cement-stabilized and solidified wastes, once the treated wastes have been buried in diverse environmental settings. Yet for lack of better tests, they continue to be used and cited.

The same environmental factors that affect the durability of concrete must be considered when evaluating the durability and permanence of cement-stabilized and solidified wastes that later are buried, either on site or off site in hazardous waste landfills. Viewed mineralogically, solidified and stabilized wastes, like hardened concrete, are metastable, both physically and chemically under ambient conditions of service. All through its service life, hardened cement and concrete attempt to reach equilibrium with exposure conditions, which, even under the harshest environments, does not approach a relative humidity of 100% and a pH of 13. Durability of concrete is governed by the material's quality and the harshness of the environmental conditions to which it is exposed over its service life. Even the best-quality concrete cannot be expected to last for centuries under extremely harsh conditions. Therefore, when considering the durability and permanence of solidified and stabilized wastes, the expected service life of such treated wastes must be defined. The service life will naturally depend on the site-specific conditions of the environment in which the treated wastes are placed. Detrimental environmental factors affecting the long-term performance and durability of solidified and stabilized wastes can only be evaluated through mineralogical evaluations of the treated wastes over time.

4. Conclusion and recommendations

Results of this study show that cement-based solidified and stabilized wastes are vulnerable to the same physical and chemical degradation processes as concrete and other cement-based materials. After the treated wastes had undergone 6 years of exposure to various environmental conditions, the extent of physical and chemical weathering of the treated wastes was evaluated. The physical and chemical alteration processes identified included freeze-thaw, carbonation, alkali-aggregate reaction, and sulfate attack on the solidified and stabilized metal-bearing wastes. The vulnerability of the treated wastes to chemical and physical attack depends to a large extent on factors such as permeability, chemical and mineralogical composition, and microstructure of the cement paste, as well as the cement and waste aggregates. Aggressive solution attack on cement-based materials results in secondary mineralization that ultimately may decompose a concrete or treated waste structure. Although the extent of degradation of the treated wastes after 6 years is considered only slight to moderate, the consequences are significant if one considers that concrete can disintegrate completely over a period of 50 to 100 years, or less.

Future studies should incorporate the results of these findings into models that evaluate the durability and permanence of solidified and stabilized wastes on the basis of actual physical and chemical weathering and alteration changes that occur in the environmental setting in which the treated wastes have been placed. It must be emphasized, however, that such models cannot be based on leaching and chemistry analyses alone; the use of all levels of microscopic analyses must be included in such studies. The advantage of micromorphic and mineralogical analyses in evaluating the effects of weathering on solidified and stabilized wastes is the ability to observe the exact area of analysis without destroying the character of the sample being analyzed, as is the case in bulk chemistry and leaching analyses. These microscopic and mineralogical analyses also show specifically what is being altered, the mode of alteration, alteration pathways, and secondary products of alteration. Such findings are important in evaluating the permanence and leaching potential under given environmental conditions. The development of such models also must be site-specific because the environmental conditions of deposition will vary.

Further, the service life of concrete-based materials depends on the nature of the environment in which it is placed. Regulations for the on-site burial of solidified and stabilized wastes, even after they are rendered nonhazardous, are needed. Adverse environments may promote or accelerate the physical and chemical decomposition of the cement matrix, releasing contaminants into the environment, or affect the mobility of certain metals that are either chemically bound or encapsulated. Burial of cement-based solidified and stabilized wastes in deleterious environmental zones, such as acid or saline soils, as well as fluctuating groundwater systems, are not recommended.

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