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## Evaluation of Sulfur Polymer Cement as a Waste Form for the Immobilization of Low-Level Radioactive or Mixed Waste

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Chemical Technology Division

**EVALUATION OF SULFUR POLYMER CEMENT AS A WASTE FORM FOR  
THE IMMOBILIZATION OF LOW-LEVEL RADIOACTIVE OR MIXED WASTE**

C. H. Mattus  
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## ACRONYMS AND INITIALISMS

BNL	Brookhaven National Laboratory
DOE	U.S. Department of Energy
INEL	Idaho National Engineering Laboratory
NRC	Nuclear Regulatory Commission
PC	portland cement paste
PCC	portland cement concrete
RCRA	Resource Conservation and Recovery Act
SC	sulfur concrete
SPC	sulfur polymer cement
TCLP	Toxicity Characteristic Leaching Procedure



## EXECUTIVE SUMMARY

Sulfur polymer cement (SPC), also called modified sulphur cement, is a relatively new material in the waste immobilization field, although it was developed in the late seventies by the Bureau of Mines. The physical and chemical properties of SPC are interesting (e.g., development of high mechanical strength in a short time and high resistance to many corrosive environments). Because of its very low permeability and porosity, SPC is especially impervious to water, which, in turn, has led to its consideration for immobilization of hazardous or radioactive waste. Because it is a thermosetting process, the waste is encapsulated by the sulfur matrix; therefore, very little interaction occurs between the waste species and the sulfur (as there can be when waste prevents the set of portland cement-based waste forms).

At present, only a limited number of studies have been performed with SPC for waste immobilization, most of which were by Brookhaven National Laboratory (BNL) on four waste streams: incinerator ash, sodium sulfate salt, boric acid, and ion exchange resins. Laboratory waste forms containing these wastes passed all Nuclear Regulatory Commission requirements for radioactive waste forms; however, full-scale testing continues at Idaho National Engineering Laboratory where operations and engineering aspects of the process are being studied. Reports indicate that, while some new problems are being uncovered, much progress is also being made. SPC has been studied in Europe by researchers from The Netherlands. In general, their finding corroborates those of BNL, showing a low leachability of radioactive tracers from the sulfur matrix.

While SPC does have promising properties, some restrictions do exist that can limit its use, especially since a prospective waste must contain less than 1% water. In addition, the question of long-term durability of this material remains unanswered because regulatory tests do not yet include data on bacteria attacking the sulfur. The fact that elemental sulfur exists only in a very narrow thermodynamic stability field and is also not found at the surface of the earth indicates that this question of long-term stability for SPC must be answered in considering this material for immobilization of low-level or mixed wastes.



## 1. INTRODUCTION

This document outlines the advantages and disadvantages of using sulfur polymer cement (SPC) as a material for immobilization of low-level or mixed wastes. Open-literature publications on this topic were reviewed. Such information is necessary to evaluate options and to determine the possibility of using this matrix for the Oak Ridge Federal Facility Compliance Agreement project in lieu of, or in combination with, other processes such as portland cement or glass.

To understand the advantages and disadvantages of using SPC for the immobilization of low-level radioactive or mixed waste, several papers were reviewed, the majority of which were issued by Brookhaven National Laboratory (BNL), the site that developed this process for the immobilization of low-level radioactive wastes [1]. To obtain a broader understanding of the material, the process, and observed properties, other sources were also searched.

Sulfur polymer cement is a relatively new material developed originally by the Bureau of Mines in the seventies. The concept of using sulfur for the immobilization of low-level radioactive wastes was studied by BNL researchers who issued numerous publications on the topic. Recently, SPC was considered by Idaho National Engineering Laboratory (INEL) for the immobilization of mixed waste in their Mixed Waste Treatment Facility project. Results of pilot-plant-scale testing and treatability studies using mixed wastes are published by INEL researchers, while laboratory-scale tests on mixed or radioactive wastes were issued by BNL.

To prevent confusion, terms found in various publications on the topic are further defined here. White SPC is the initialism for sulfur polymer cement, SC is that for sulfur concrete. Once loaded with aggregates or waste products, the original material SPC becomes SC. This nomenclature follows the same principle as that for portland cement. The paste of neat portland cement is represented by PC, while the concrete obtained by the addition of sand and aggregates to PC is designated by PCC, or portland cement

concrete. Some publications, especially those originating from BNL, use the terminology “modified sulfur cement” instead of SPC as found in other reviewed publications; however, both names refer to the same material.

## 2. MATERIAL AND TECHNIQUE

Sulfur has a large number of allotropic forms. The melting point of sulfur is within the range of 112.8°C (rhombic form) to 120.0°C (amorphous form). The specific gravity is 1.96, 2.046, and 2.07 for monoclinic, amorphous, and rhombic sulfur respectively. The boiling point for all forms is 444.7°C.

The more common form,  $\alpha$ -sulfur, is rhombic and at 95.5°C undergoes transition to  $\beta$ -sulfur, which is monoclinic. This transformation is associated with a volume change and residual stresses in the final product due to the higher density of the  $\alpha$ -form [2]. The physical properties and final shrinkage of the sulfur-based materials were found to be incompatible with commercial objectives, for tests such as thermal cycling could result in final form disintegration when the sulfur is not used with stabilizing admixtures.

The Bureau of Mines initially studied this material to determine its value in repairing construction edifices such as bridges and roads. They studied and overcame shrinkage problems associated with cooling by finding admixtures that prevented this phenomenon. They added 5% admixtures (i.e., dicyclopentadiene and oligomers of cyclopentadiene added in equal amounts) to the sulfur and created a modified sulfur cement that is now commercially available as SPC. This material possesses several interesting properties, the most important of which are its rapidly achieved high mechanical strength and its high resistance to corrosive environments. SPC has a viscosity at 135°C of  $50 \pm 25$  cp and a specific gravity at 25°C of  $1.90 \pm 0.02$ . Table 1 provides data on the composition and properties of SPC; Table 2 shows the resistance of SPC to various chemical species.

**Table 1. Composition and properties of sulfur polymer cement**

Species or property	Value
Sulfur, %	95 ± 1
Carbon, %	4.5 ± 0.2
Hydrogen, %	0.5 ± 0.05
Viscosity at 135°C, cp	50 ± 25
Specific gravity at 25°C	1.90 ± 0.02

*Source:* McBee, C. W., and Weber, H. H., "Sulfur Polymer Cement Concrete," in *Proceedings of the Twelfth Annual Department of Energy Low-Level Waste Management Conference*, CONF-9008119, National Low-Level Waste Management Program, Idaho National Engineering Laboratory, Idaho Falls, Idaho, 1990.

**Table 2. Properties of typical sulfur concrete and portland cement concrete**

	Sulfur concrete <sup>a</sup>	Ordinary portland cement concrete <sup>b</sup>
Strength, psi		
• Compressive	7,000–10,000	3,500–5,000
• Splitting tensile	1,000–1,500	500
• Flexural	1,350–2,000	535
Coefficient of thermal expansion ( $\mu\text{in./in.}/^\circ\text{C}$ )	14.0–14.7	12
Moisture absorption, %	0.0–0.10	0.30–3.0
Air void content, %	3.0–6.0	4.0
Elastic modulus, $10^6$ psi	4.0	4.0
Specific gravity	2.4–2.5	2.5
Linear shrinkage, %	0.08–0.12	0.06–0.10
Impact strength, ft-lb		
• Compressive	100–119	81
• Flexural	0.3–0.5	0.2
Mix proportions, wt %		
• Sulfur polymer cement	14–18	0
• Water	0	6–9
• Mineral filler	6–9	0
• Portland cement	0	12–18
• Sand	38–42	30
• Coarse aggregate	33–37	45

<sup>a</sup>Properties obtained at age of 1 day.

<sup>b</sup>Properties obtained at age of 28 days.

*Source:* McBee, C. W., and Weber, H. H., "Sulfur Polymer Cement Concrete," in *Proceedings of the Twelfth Annual Department of Energy Low-Level Waste Management Conference*, CONF-9008119, National Low-Level Waste Management Program, Idaho National Engineering Laboratory, Idaho Falls, Idaho, 1990.

In the application of immobilization of radioactive or mixed wastes, the use of SPC is considered to be an encapsulating process. Little direct interaction occurs, except for some sulfide-forming metals, between the waste and the sulfur to bind hazardous or radioactive species chemically with the matrix such that their diffusivity to the environment is reduced. The immobilization concept of this process is to entrap the waste particles in the sulfur matrix and to immobilize them physically [3][4]. However, in the case of incinerator ashes, Darnell et al. [5] state that some metal oxides found in fly ash resulting from the combustion of mixed wastes are chemically bonded to SPC since they "are converted to less soluble metal sulfides and a small percentage of sulfates." This property of SPC to transform mercury, cadmium, and lead oxides to less soluble sulfide forms is also reported by Mayberry et al. [6].

When comparing the properties of sulfur and portland cement matrices for immobilization of mixed wastes, SPC is known to be impervious to water, while PC is a fairly porous material. One interesting point is that SC and PCC have approximately the same volume of void space (i.e., pores); however, the pores in SPC concrete are not connected (providing impermeability), while the pores of PC concrete are connected (making the waste form permeable) [4]. Table 3 summarizes some of the performance data for SPC when tested in industrial environments and illustrates the impermeability (and in some cases, the reactivity) of this material.

Table 3. Industrial testing results of sulfur concrete materials

Environment	Performance <sup>a</sup>
Sulfuric acid	Nonreactive
Copper sulfate-sulfuric acid	Nonreactive
Magnesium chloride	Nonreactive
Hydrochloric acid	Nonreactive
Nitric acid	Nonreactive
Zinc sulfate-sulfuric acid	Nonreactive
Copper slimes	Attacked by organics used in processing
Nickel sulfate	Nonreactive
Vanadium sulfate-sulfuric acid	Nonreactive
Uranium sulfate-sulfuric acid	Nonreactive
Potash brines	Nonreactive
Manganese oxide-sulfuric acid	Nonreactive
Hydrochloric acid-nitric acid	Nonreactive
Mixed nitric-citric acid	Nonreactive
Ferric chloride-sodium chloride-hydrochloric acid	Nonreactive
Boric acid	Nonreactive
Sodium hydroxide	Attacked by >10% NaOH
Citric acid	Nonreactive
Acidic and biochemical	Nonreactive
Sodium chlorate-hypochlorite	Attacked by solution at 50 to 60°C
Ferric-chlorate ion	Nonreactive
Sewage	Nonreactive
Hydrofluoric acid	Nonreactive with graphite aggregate
Glyoxal-acetic acid formaldehyde	Nonreactive
Chromic acid	Deteriorated at 80°C and 90% concentration; marginal at lower temperature and concentration

<sup>a</sup>Test results show no sign of corrosion or deterioration for test period of 6 to 9 years.

Source: McBee, C. W., and Weber, H. H., "Sulfur Polymer Cement Concrete," in *Proceedings of the Twelfth Annual Department of Energy Low-Level Waste Management Conference*, CONF-9008119, National Low-Level Waste Management Program, Idaho National Engineering Laboratory, Idaho Falls, Idaho, 1990.

### 3. ADVANTAGES AND DISADVANTAGES OF SULFUR POLYMER CEMENT OR SULFUR CONCRETE AS DESCRIBED IN THE LITERATURE

Very little information is available on SPC since it is a relatively new material. The Bureau of Mines have provided data on most of the major properties of SPC. BNL primarily studied the potential use of this material with radioactive and mixed wastes. INEL publications essentially cover full-scale testing of SPC for immobilization of mixed waste, and a few papers from Europe describe using SPC for radioactive and/or mixed waste immobilization. Only one publication was found related to using SPC in a treatability study.

K. L. Gering [7] of INEL reports on treatability studies for mixed waste immobilization at INEL using two types of matrices: PC and SPC. Among the nine waste streams studied, including liquids, sludges and solids, seven were stabilized using PC and two using SPC. An experimental design matrix was used for this treatability study, and the two criteria studied for acceptability of the waste forms were the TCLP and free liquid test. Among all the formulations tested (92 for portland cement) only three failed the TCLP; the same number of SPC-waste forms failed the TCLP, while no waste form with either binder was found to generate free liquid as defined by EPA Method 9095.

Gering concludes that some of the wastes studied appear to be better suited for one matrix than for the other. He stated that one waste selected for SPC immobilization which contained about 50% water consumed much time and energy in order to obtain the necessary dry condition prior to addition to the sulfur matrix. Also this dried waste had a low density resulting in problems of flotation of the particles above the molten SPC. His results showed that one process or matrix cannot handle all the waste streams.

Characterization of the waste should help in deciding which process is better suited for the waste stream; factors to be considered are moisture content, waste composition, and

known incompatibility of some waste species with one particular process or matrix. Bench-scale treatability studies obtained satisfactory results with both matrices, and results illustrate the fact that a "perfect" matrix capable of accepting all types of waste is not yet available.

The SPC process is still at the development-scale stage; however, some publications were found describing full-scale test performed by INEL [5][8][9]. Darnell from EG&G Idaho, INEL [8], is heading the full-scale development of this process as is described in a trip report written by Snider [9] of Oak Ridge, who assisted in a third test performed on February 2-3, 1993 at Bethlehem Corporation, Easton, Pennsylvania. The conclusions of these tests can aid in appreciating the engineering problems that must be overcome for effective use of such a process.

### **3.1 ADVANTAGES**

#### **3.1.1. Physical and Chemical Properties**

Notable SPC physical and chemical properties include durability in corrosive environments, mechanical strength, corrosion and freeze-thaw cycling resistivity, radiation-shielding properties, and low permeability and porosity. These are discussed as follows:

1. SPC is resistant to mineral acids and high salt environments [2], and it also resists corrosive electrolyte attack [3][4]. Table 3 summarizes test results obtained with sulfur concrete materials. As a result, some researchers predict that SPC could have twice the durability of PC [3]; they base their conclusion on the impervious nature of the material compared with PC. This statement may be true only if all the necessary steps are taken to prevent open porosity from forming in the waste form; this topic is discussed further in this study.
2. High mechanical strength is achieved rapidly upon solidification, for about 80% of the final strength is achieved in only a few hours and full strength is achieved within 30 days [2]. This property is based on sulfur containing no waste. Testing of waste forms

generated during treatability studies could be performed after 5 days using SPC, while 28 days were necessary for PC [7].

3. SPC is very impervious to water [4]; however, if dried salt crystals are exposed at the surface of the waste form, they can attract water and provoke cracking and swelling of the waste form resulting in possible destruction due to expansion of some hydrating salt crystals. SPC also does not react with steel [4]; therefore, no corrosion of containers is expected. The linear shrinkage, 0.1%, is comparable with that of PC. SPC is also resistant to freeze-thaw cycling, generating a comparable coefficient of expansion with PC concrete [4]; additionally, creep for SPC is about half that for PC concrete [4].
4. SPC has a comparable density with that of hydrated PC; therefore this material should provide similar radiation-shielding properties [3].
5. The SPC matrix has low permeability and porosity, properties that produce the impervious nature of this material to water. However, Van Dalen [10] indicates that the porosity depends strongly on the nature of the incorporated waste, for he measured porosities ranging from 0.1 to 50%.

### **3.1.2 Operational Characteristics**

SPC operational characteristics include greater flexibility, easier cleaning operations, and less volatilization potential compared with other waste forms. These are discussed as follows:

1. Compared with PC, SPC has greater flexibility. Once water is added to PC, only a few hours are available for using the mixture; then it will become hard and cannot be used any longer. With SPC, even if the material were heated, it could remain hot for a long time in the mixer. During their preliminary full-scale testing, INEL researchers let a 1-m<sup>3</sup> mold full of SPC remain hot for several hours, leaving 5 h to fill the mold. During this time, they did, however, observe a separation of ash from the sulfur mixture, which became apparent by the flotation of ash particles above the molten matrix [5] for ashes of a lower density.

The advantage of being able to reheat SPC that had cooled in a mixer for reuse later was also mentioned [2]. INEL was planning on performing this reheat test [5], but such an operation does not appear to be as easy as implied, considering the narrow temperature window that can be safely used with sulfur. However, Snider discusses a full-scale test successfully performed in February 1993 under the supervision of Darnell [9].

2. Cleaning operations of the mixer after one campaign should be easier than when using PC; even if some material remains in the mixer, it will be remelted during the next campaign. Also no contaminated rinse water is generated from cleaning operations [4]. However, when working with mixed wastes having different waste codes and different hazardous characteristics, one may not want to have cross-contamination of hazardous species; therefore, cleaning could become a necessity for mixed waste. This operation could be problematic depending on the type of mixer employed and the waste types.
3. Because of the relatively low operational temperature, volatilization of many hazardous species should not occur, especially compared with glass waste forms [6].

### **3.1.3 Waste Stream Compatibility and Waste Loading**

SPC has the potential for maximum to superior waste loading for some problematic waste species, no interaction of waste components that could prevent solidification using some waste streams, and less demanding chemical analysis requirements. These are discussed as follows:

1. SPC could be the answer for those problematic waste species that are difficult to immobilize in PC matrices such as boric acid salts, very high salt laden concentrates, and sodium sulfate salts [3]. When such wastes are immobilized, SPC performance, compared with that of PC, shows a greater advantage in maximum waste loading for these particular species (see Table 4) [3][11][12][1]. However, note that high salt loadings can lead to major problems (see Subject. 3.2.3), and that a limited number of waste streams were studied. Van Dalen and Rijpkema [10] give some limitations of the waste types that can be incorporated in an SPC matrix. The preferred waste streams are inorganic, low-solubility compounds such as sludges, precipitates, and incinerator ash,

while organic materials, ion exchangers, and highly soluble compounds should be avoided.

2. A demonstration of the superior waste loading achievable using the SPC matrix, compared with the PC matrix, was made by BNL researchers [1]; their results are presented in Table 5. They found that limitations exist for the incorporation of some types of waste streams. They studied four types of wastes commonly produced by the nuclear industry that usually present problems for immobilization in PC matrices: sodium sulfate salts, boric acid wastes, incinerator ash, and ion exchange resins. Their study consisted of two phases. First, they determined the maximum waste loading that could be achieved using the sulfur matrix without considering the final required properties of the waste form. During this phase they also compared the effects of using two different types of mixers upon the waste loading. A dual action mixer obtained the best results for all the wastes studied, when compared with an extruder, on the laboratory scale. Table 4 summarizes the maximum waste loadings that they could achieve in an SPC matrix using both kinds of mixers and the four selected waste streams.

**Table 4. Summary of maximum waste loadings for modified sulfur cement waste forms achieved during process development studies**

Waste type	Max. loading by extrusion (wt %)	Max. loading by dual action mixer (wt %)
Sodium sulfate	65	80
Boric acid	40	57
Incinerator ash	20	43
Ion exchange resin	40	NA <sup>a</sup>

<sup>a</sup>Not applicable owing to destruction of the waste form during the immersion test.

Source: Arnold, G., et al., *Modified Sulfur Cement Solidification of Low-Level Wastes*, BNL 51923, Brookhaven Nat. Lab., Upton, N.Y., 1985.

Second, they focussed on the evaluation of the waste form properties for these four waste streams. They tested compressive strength (ASTM C-39), water immersion (90 days, ASTM C-39), thermal cycling (ASTM D-621, C-39), and leaching (ANS 16.1, 90 days) of the

numerous waste forms generated using a wide range of waste loading. As a result, they were able to determine the maximum waste loading achievable in a waste form that could still meet the Nuclear Regulatory Commission (NRC) and the U.S. Department of Energy (DOE) requirements. Table 5 provides the optimum recommended waste loadings for an SPC matrix for the specific waste types, as well as a comparison of the waste loading that the BNL researchers achieved in the past with the same waste, when using a PC matrix.

**Table 5. Comparison of optimal recommended waste loadings for modified sulfur cement and portland cement based on processing and waste form performance considerations**

Matrix	Sodium sulfate	Boric acid	Incinerator ash	Ion exchange resins
Solidification in modified sulfur cement				Not recommended
•Wt % waste loading <sup>a</sup>	40	40	43	
•55-gal. drum, kg <sup>b</sup>	415	287	384	
•Waste/drum, kg <sup>c</sup>	166	115	182	
Solidification in hydraulic portland cement				
•Wt % waste loading <sup>a</sup>	9	15	40	13
•55-gal. drum, kg <sup>b</sup>	307	296	318	318
•Waste/drum, kg <sup>c</sup>	28	44	127	41

<sup>a</sup>Based on dry solid weight.

<sup>b</sup>Drum size waste form.

<sup>c</sup>Equivalent quantity of waste that can be incorporated in 55-gal drum waste form.

Source: Arnold, G., et al., *Modified Sulfur Cement Solidification of Low-Level Wastes*, BNL 51923, Brookhaven Nat. Lab., Upton, N.Y., 1985.

With the optimum waste loadings, as they appear in Table 5, BNL researchers achieved their goal of producing a waste form with properties that could meet almost all NRC and DOE requirements. However, no tests of the long-term performance, after 90 days, were performed.

3. Kertesz et al. [13] in Cadarache, France, compared SPC with other matrices (cement, epoxy resin, and cement + epoxy resin) for the immobilization of incinerator ashes containing alpha emitters as high as 50 Ci/metric ton. They performed their work in laboratory glove boxes, allowing them to work with the actual ashes. J. Rijpkema of The Netherlands assisted by sharing his experience in handling and working with SPC with Kertesz and his coworkers. Using nonradioactive ashes, Kertesz et al. at first performed scoping tests to determine the waste loading that SPC could accept with their particular ashes. A weight loading of 25% was found to be achievable.

In their tests, the reactor and the ashes were first heated to 150°C, and the SPC was added by successive additions over 15 min while the temperature was maintained at between 120 and 130°C. The receiving molds were heated, and after the pour, the samples were transferred to a 120°C oven, where the temperature was slowly lowered to ambient over 5 h. The researchers poured three 200-g samples for their leaching tests, at 25 wt % ash and initial waste activities of about  $9 \times 10^7$  Bq.

The leaching tests were performed over 6 months, and the fractional releases for the three SPC samples were found to be between  $3 \times 10^{-3}$  and 0.5. Kertesz et al. compared these results with those obtained with the other matrices that were studied: that is,  $5 \times 10^{-5}$  for OPC cement,  $1 \times 10^{-5}$  for epoxy resin, and  $7 \times 10^{-6}$  for epoxy resin + cement. They noticed that during the first week of leaching, the SPC samples began to spall, with some small pieces of the waste form reporting to the bottom of the container. This tendency of SPC to spall was not observed after the first week.

4. Because this is a thermosetting process, no interaction of waste components prevents solidification as is the case with PC [3], whose mechanisms of hydration can be inhibited or stopped completely by some waste species. However, some waste streams are not recommended for immobilization using this process (see Subsect. 3.2.2) [4]. SPC has been tested as a waste form with only a small number of waste streams. Only four types were tested by BNL researchers (see Tables 4 and 5); among those waste streams, none produced interferences for the set of the material by inhibiting the hardening process.

5. Chemical analysis requirements for the waste being considered for immobilization are less demanding for SPC than for other processes [4] because most wastes have no known major chemical reaction with the sulfur matrix.

#### **3.1.4 Immobilization of Hazardous Wastes in SPC**

SPC waste forms appear to pass Toxicity Characteristic Leaching Procedure (TCLP) tests when hazardous wastes are immobilized in them [4][12]. Kalb et al. [14] reported results of a study using incinerator fly ash containing 36 wt % zinc (as zinc chloride), 7.5 wt % lead, 0.7 wt % copper, and 0.2 wt % cadmium. The tested SPC form had TCLP concentrations for lead and cadmium above the U.S. Environmental Protection Agency regulatory limits. By adding 7 wt % sodium sulfide to 50 wt % SPC and mixing it with 43 wt % fly ash (optimal formulation), the waste form was able to pass the TCLP test for these species. A comparison of the maximum achievable waste loading in SPC and PC matrices when using this particular waste was made. A waste loading of 55% fly ash in the SPC matrix was possible, while only 16% could be incorporated in the PC matrix [14].

A chemical reaction between mercury and lead is present in waste that can form lead and mercury sulfides (insoluble forms for these metals) when immobilized in SPC [4]. No data were found, related to waste immobilization, that could prove if this chemical reaction is complete or partial by just encapsulation or adsorption of the waste metals on sulfur. Darnell et al. [5] state that heavy metal oxides present in a mixed waste incinerator ash are bound chemically to SPC and form "less soluble metal sulfides and a small percentage of sulfate." To obtain such a reaction, it is necessary to have enough free sulfide in the sulfur; elemental sulfur cannot, by itself, form sulfide with these metals. The example given in the above paragraph corroborates the fact that, to be able to combine all the lead from his waste and form lead sulfide, Kalb had to add sodium sulfide to SPC to pass the TCLP.

Various techniques could (1) provide information about the chemical form of the Resource Conservation and Recovery Act (RCRA) metals after immobilization in SPC and (2) indicate if these metals are still under oxide form or if they are transformed into sulfide or sulfate

forms. It would have been interesting to obtain such data to prove that SPC acts to stabilize such metals. With the data available, SPC appears to rely upon encapsulation of the waste in the sulfur matrix for most of the RCRA metals.

Tests performed in The Netherlands by Van Dalen [10] provide some insight as to the possibility of sulfide formation between metals and SPC. Strips of lead, stainless steel, aluminum, copper, and brass were dipped in the molten SPC, and the formation of a dark layer of metal sulfide was observed for those metals that have a higher affinity for sulfur than oxygen (i.e., lead, copper, and brass). The intent of their test was to determine if SPC could be used as temporary storage of activated metal components with short-lived radioisotopes.

If some possibility of forming metal sulfides with SPC does exist, it is well known that metals precipitated as sulfides are more stable than when precipitated as hydroxides. In PC-based waste forms, many metals form higher solubility hydroxide forms. Table 6 presents the theoretical solubilities of hydroxides and sulfides of selected metals in pure water at standard conditions. It also shows which metals are able to form highly insoluble sulfides.

### **3.1.5 NRC Requirements for SPC Waste Forms**

While test results, biodegradation data, and parameters permitting full-scale use of SPC for the immobilization of low-level wastes are promising, more biodegradation studies are in progress and some engineering questions remain. These are discussed as follows:

1. All NRC requirements, except for full-scale tests, appear to have been passed successfully. Compressive strength, immersion tests, leach tests, biodegradation, thermal cycling, and irradiation tests have already been performed successfully on some waste forms [4][12][15]; the waste streams used during these tests are presented in Tables 4 and 5. Because the waste form does not contain water, there is no risk of gas generation during the irradiation test. Van Dalen [10] indicates that up to 20 MGy, no gaseous radiolysis occurred and that the mechanical strength of the SPC increased after the waste form was irradiated. However, some other risk of degradation of the waste form can occur (see Subjects. 3.2.3 and 3.1.3). The results obtained by Van Dalen [10] indicate

that the leaching of radionuclides is low owing to low permeability and diffusivity of the material. The normal ANS 16.1 leaching test appears to be too short for this type of material to obtain meaningful results.

**Table 6. Comparative solubilities of metal hydroxides and sulfides**

Metal	Solubility of metal ions (mg/L)	
	As hydroxides	As sulfides
Cadmium (Cd <sup>2+</sup> )	2.3 × 10 <sup>-5</sup>	6.7 × 10 <sup>-10</sup>
Chromium (Cr <sup>3+</sup> )	8.4 × 10 <sup>-4</sup>	No precipitate
Cobalt (Co <sup>2+</sup> )	2.2 × 10 <sup>-1</sup>	1.0 × 10 <sup>-8</sup>
Copper (Cu <sup>2+</sup> )	2.2 × 10 <sup>-2</sup>	5.8 × 10 <sup>-18</sup>
Iron (Fe <sup>2+</sup> )	8.9 × 10 <sup>-1</sup>	3.4 × 10 <sup>-5</sup>
Lead (Pb <sup>2+</sup> )	2.1	3.8 × 10 <sup>-9</sup>
Manganese (Mn <sup>2+</sup> )	1.2	2.1 × 10 <sup>-3</sup>
Mercury (Hg <sup>2+</sup> )	3.9 × 10 <sup>-4</sup>	9.0 × 10 <sup>-20</sup>
Nickel (Ni <sup>2+</sup> )	6.9 × 10 <sup>-3</sup>	6.9 × 10 <sup>-8</sup>
Silver (Ag <sup>+</sup> )	13.3	7.4 × 10 <sup>-12</sup>
Tin (Sn <sup>2+</sup> )	1.1 × 10 <sup>-4</sup>	3.8 × 10 <sup>-8</sup>
Zinc (Zn <sup>2+</sup> )	1.1	2.3 × 10 <sup>-7</sup>

*Source:* Grosse, D. W., "Review of Treatment for Hazardous Waste Streams," Chap. 21 in *Encyclopedia of Environment Control Technology, Vol. 4, Hazardous Waste Containment and Treatment*, EPA/600/D-91-/088, Environ. Protection Agency, 1991.

- It is stated that biodegradation promoted by thiobacilly bacteria does not appear to present a problem for SPC. This bacteria, on the other hand, is known to attack and to destroy PC [4] as is stated by researchers of the University of Hamburg who declared that "cement-stabilized construction materials are disintegrated by thiobacilli, liberating sulfuric acid as a metabolic product; sulfuric acid reacts with the calcium components of

the cement and transforms into gypsum.” This statement does not, however, specify the conditions under which such degradation could occur.

Lea [16] and Taylor [17] discuss the potentiality of bacterial attack on cement paste or concrete. This attack is limited only to special conditions or environments such as in sewage where anaerobic bacteria can be active and lead to the formation (as a final product) of sulfuric acid, which destroys the concrete. Other examples where the result of bacterial attack is observed and leads to the formation of sulfuric acid are in cooling towers and concrete floors laid on rocks containing pyrites. Both authors, however, mention that at a pH of 10 or above, which is the usual pH of interstitial pore water in cement pastes or concrete, the bacterial activity is severely decreased or absent.

Following the standard ASTM G-21 and ASTM G-22 tests, BNL researchers tested samples of modified sulfur cement containing no waste for bacteria or fungi to attack. These tests had a duration of 21 days, and even though ideal conditions for the growth of bacteria or fungi were applied (i.e., incubation at 35 to 37°C, moist atmosphere with relative humidity  $\geq 85\%$ , and presence of a nutrient agar to sustain growth), no evidence of microbial growth was present at the completion of the test. However, more studies are in progress to verify several other thiobacillus strains that could have some potential action on metabolizing sulfur-based materials [15]. Van Dalen [10] reports that phosphate is among the most important nutrients necessary for bacterial action on sulfur. Some bacteria are actually found to attack elemental sulfur, and several publications on the topic illustrate that this material is sensitive to biodegradation [18][19].

3. Preliminary tests were performed to select the important parameters permitting full-scale use of SPC for the immobilization of low-level wastes [4] or mixed wastes [5]. Results point to the engineering issues that must be solved such as finding a mixer with a heated bowl and paddle as well as “using a weir instead of a valve to avoid flow control problems.” Already, BNL researchers have made a comparison during the bench-scale testing phase by using an extruder or a dual action mixer; the latter is more appropriate for this material [1]. They raised some concerns about issues other than the mixer for larger-scale testing. Considering the cooling of this material, the transfer of the molten

mixture to the mold seems also to be an important parameter. The molds have to be heated and able to control the cooling phase of the waste form, which is known to be one of the most important parameters for obtaining an impermeable final product. Formation of voids in the waste form seems to be a concern in some cases [1] as well as when the sulfur cools too quickly.

### **3.1.6 Engineering Developments Related to SPC Full-Scale Testing**

BNL researchers were unable to perform the full-scale test required by NRC for approval by this commission of the new process owing to the size of their laboratory-scale mixer. INEL researchers, however, performed full-scale tests that always included pouring the fly ash and SPC mix over coarse bottom ash and pipes of various sizes to determine the filling efficiency of voids by cross-sectioning and observation afterwards. This was performed by pouring 18 kg (40 lb) of incinerator ashes (> 3/8 in.) into a 3 × 3 × 2.66 ft container that also had steel pipes of different diameters lying horizontally and two pipes standing vertically. In each test, the SPC concrete was prepared by mixing 40 wt % incinerator ash (< 3/8 in.) with 60 wt % SPC and then pouring the molten mixture over the ash and pipe arrangement in the container.

#### **3.1.6.1 Test performed in 1991**

The mixer used during the test [5], a Holo-Flite Processor, allowed heating of both the exterior and the inside of the mixer. The mixing operation was continuous from the entry to the exit of the mixer. INEL researchers concluded, however, that the mixer would have to be modified for better efficiency by the addition of (1) a mixing lug to each flite to improve the blending of the SPC with the fine ash and (2) computerized instruments to control and to maintain the heat of the mixture, which should remain at  $135^{\circ}\text{C} \pm 6^{\circ}\text{C}$ . At temperatures below  $128^{\circ}\text{C}$ , hard solidified blocks of material are formed, while at temperatures above  $150$  to  $160^{\circ}\text{C}$  (the sources do not agree on the temperature at which this reaction occurs), SPC starts emitting hydrogen sulfide gas. When this happens, the properties of the materials are altered such that pouring becomes impossible. Other parameters would have to be computer-

controlled as well (e.g., shaft speed, input SPC temperature, input ash temperature, container and its content temperature, and weir height).

The container that will receive the molten SPC mixture, as well as its contents, must be heated prior to pouring and during operations at 135°C. If not, voids will form in the waste form and, as a result, cause it to lose its impervious properties and also induce thermal stress cracks in the final form.

The ash that is incorporated in the SPC must be extremely dry. The water content of the ash was measured at 0.2%, but a content of 0.0% is the operational goal.

There is a risk of flotation of waste or ash particles in the drum during the pour. If the mixture remains molten long enough, the lower density particles (i.e., ash) can move upward to the top of the molten SPC. This segregation jeopardizes the homogeneity and properties of the final waste form.

The engineers who performed the test concluded that using a valve for controlling the pour is not reliable enough when dealing with low-level or mixed waste immobilization. Therefore, they suggested replacing the sprues used during this test by weirs. Also, the weir would have to be welded in place, and the whole mixer would be lifted prior to pouring, to reduce the risk of malfunction if the weir were able to move.

The processing rate for producing the waste form would have to be accelerated, for in this preliminary test, it took 5 h to fill a 1-m<sup>3</sup> container.

#### **3.1.6.2 Test performed in 1992**

Two pours were performed during the summer of 1992 using the Holo-Flite equipment of Denver Equipment Company located at Colorado Springs [8]. In these tests, the contents of the mold, as well as the container, were heated to about 130°C prior to and during the pour and for many hours after the pour. The ashes at the bottom were heated to only 107°C. The time required to perform the pour was decreased considerably, dropping from 4 h to 1 h and

50 min for test 4 and 1 h and 15 min for test 5. Test 4 did not reach the top of the mold because of excessive surface cooling that solidified the upper surface. Forty-one thermocouples placed in the waste form showed the temperature of the molten SPC to be homogeneous during the pour. The pipes placed horizontally inside of the mold were not filled completely toward the upper part of the mold and therefore contained voids.

Test 5, in which the pour was faster, also had the container and contents heated prior to and during the pour; the temperature was slightly higher (5°C) than that for test 4. The ashes on the bottom, however, were heated to 121°C as part of some engineering modifications to improve this test. The voids present inside of the pipes were decreased significantly, and the box was filled completely without shrinkage.

### **3.1.6.3 Test performed in 1993**

In a trip report dated February 2-3, 1993, Snider [9] reports his observations as a witness of another full-scale immobilization of hearth ash in SPC at Bethlehem Corporation, Easton, Pennsylvania. At this time, Darnell from INEL was testing, the Beaver Tail Mixer, an oil-heated mixer, manufactured by Bethlehem Corporation [8]. The rationale for selecting this type of mixer was that (1) its engineering features are better suited for this type of material and for the use of a mechanical weir for pouring and (2) the stronger mechanical action of this mixer to bring more particulates of metal oxide in contact with sulfur may increase the formation of metal sulfides/sulfates during the mix. During this test some of the conclusions of the last were tested: (1) the mold form contained electrical strip heaters, (2) a control panel was used to monitor the temperature of the container and mold form heaters, and (3) a weir was used to control the residence time of the molten admixture in the mixer.

The mixer employed a shell and paddles heated by hot oil circulation. Two tests were performed in which the particle size of the ash mixed with the SPC was the only variable: in test 6, ashes with a diameter of  $< 3/8$  in. were used; in test 7, 70- $\mu\text{m}$  ash was employed. The pour was continued until material overflowed the overflow sprue. The time for filling the container with the admixture was 1 h. The viscosity achieved in this mixer appeared

lower, and the SPC was more fluid than with the other mixer; also, the test using 70- $\mu$ m ash appeared to be even better.

The next morning, however, the results obtained were disappointing, for they observed a decrease of 7.6 cm (3 in.) in the level of the material in the container as well as a frothy-like crust on the surface; apparently, air-venting was not completed when the mixture solidified. Some large air pockets were also present in the waste form, the upper level pipes were not filled, and a 15% shrinkage was measured. The reason for these defects was attributed to the higher speed of the paddles, which resulted in the formation of too many air bubbles in the molten sulfur concrete. These air bubbles are, in the commercial sector, eliminated by vibration of the molten mixture. Also, the 70- $\mu$ m ash was found to be unacceptable because it became airborne. Additional tests to determine the optimum-size particles are in progress at INEL.

Test results showed that finding the appropriate mixer was not as easy as it might appear. One of Snider's comments was that this mixer was operating well; however, it seemed "to introduce excessive amounts of air in the mix." Excessive amounts of air, therefore, can affect the quality and properties of the final waste form because entrapped air bubbles will increase open porosity in the waste form. It is through the open pores, especially those present at the surface of the waste form, that water can migrate inside and increase the leachability of the hazardous or radioactive waste species that are, for the most, only entrapped in the sulfur-based matrix.

Other tests are planned for FY 1994 using the same equipment as that used during the last campaign; however, information acquired from the last tests will be translated into modifications of the engineering system to improve the final waste form produced (i.e., vibration and particle size). Darnell states that the parameters they are studying may change considering the results obtained after the first new test and that is "we are testing in an area that has very few historical data to draw from. Each new discovery influences the next test."

## 3.2 DISADVANTAGES

### 3.2.1 Temperature Control

Temperature control involves many factors: type of material, flammability, minimum and maximum temperature range, and effect on wastes that can undergo transitions. These are discussed as follows:

1. Because SPC is a thermoplastic material, the maximum operating temperature for the waste forms is 88°C [2].
2. The material will melt if exposed to temperatures above the melting point of 119°C and will lose its integrity [2]. Mayberry et al. [6] reported that a constant temperature of 100°C for the disposal environment of SPC waste forms should be considered as the maximum.
3. The material will burn if it is exposed to an open flame, but McBee and Weber indicate that it does not support combustion on its own [2]. However, SPC and SC meet none of the criteria for classification under U.S. Department of Transportation regulations as flammable material [4]. Testing was performed only on material that did not have waste incorporated in it; therefore, the effect upon the waste form combustion is unknown. The self-ignition temperature in air starts at 220°C [10] and generates toxic SO<sub>2</sub> gas.
4. McBee and Weber note that the optimum processing temperature range for SPC is between 127 and 138°C [2], while Darnell [5] suggests 129 to 141°C. Above the temperature range of 150 to 160°C, a sharp rise in viscosity occurs because of additional polymerization within SPC that makes the material "gummy and unpourable" [5]; hydrogen sulfide (H<sub>2</sub>S) gas, which is poisonous and flammable [7][20][5], also forms. Additionally, if the processing temperature is too low, the sulfur will be incompletely or partially melted. Automatic temperature and gas controls have to be used for safety reasons and process quality control (see Subsect. 3.1.6).

5. Dry wastes that can undergo transitions or water loss might present problems. BNL reports difficulties in processing boric acid waste at elevated temperatures (i.e.,  $> 169^{\circ}\text{C}$ ) related to the transformation of boric acid into meta borate with the generation of water vapor. The waste form produced was of poor quality [1] because of tiny voids extending to the surface of the waste form. These voids present a way for gas or water to enter the matrix and attack or leach immobilized waste.

### 3.2.2 Waste Stream Limitations

Waste stream limitations may involve SPC deterioration, chemical corrosion risks, inappropriate moisture content of waste, swelling and other effects of admixtures, and specific gravity of wastes. These, together with wastes not recommended as good candidates for encapsulation in an SPC matrix, are discussed as follows:

1. SPC deteriorates in hot, concentrated chromic acid solutions, hot organic solvent solutions, sodium chlorate-hypochlorite copper slimes, and strong alkalies ( $> 10\%$ )[3][4]; therefore, waste streams containing these species might not be appropriate for encapsulation in SPC. SPC can be dissolved by solvents such as carbon disulfide, bromoform, and other sulfur-dissolving solvents [10].
2. SPC is not recommended for use with strong bases and oxidizing agents, aromatic or chlorinated hydrocarbons, or oxygenated solvents because of the risk of chemical corrosion due to  $\text{H}_2\text{S}$  formation [10]. Chemical reactions may also occur when SPC is used with nitrate salts owing to the risk of combustion [3][4], especially when carbon is present.
3. The SPC matrix is not well-suited for wet waste; PC is more appropriate when the composition of the waste is compatible with PC hydration mechanisms [7]. All admixtures added to SPC must be dried prior to addition. McBee, who actually developed this process when working at the Bureau of Mines, recommended that aggregates that must be incorporated with the sulfur cement must have a moisture content less than 1% [2]. In the case of waste form production, Darnell et al. [5] reported a

0.2% moisture content for ash introduced in the SPC matrix during their full-scale test, and they recommended that the goal be 0% water to obtain a good waste form.

Mayberry et al. [6] recommended heating of the waste to at least at 200°C prior to introducing it into the sulfur matrix.

4. Admixtures like swelling clays (e.g., bentonite), ion-exchange resins, or high-salt loadings can be dangerous because of the risk of rupture of the waste form [3][2][15][1][10]. The destruction of the waste form can occur when these dry additives are absorbing moisture from the environment and then swell. Van Dalen and Rijpkema [10] also indicate that highly soluble compounds are dangerous for the integrity of the waste form. They produced waste forms containing borate wastes, and considering the results obtained by the BNL researchers using high loadings of these salts, they added 5 to 15% and still obtained cracks in the waste form because of osmotic pressure effects of the soluble salts.
5. If some admixtures are not perfectly dry, the steam produced during the mixing, and especially the cooling phase, will generate tiny vents to the surface of the waste form making it porous [3][2]. This drying operation to obtain less than 1% moisture for waste streams possessing a high moisture content can considerably increase the cost for producing a waste form, and there is a possibility that the final product may not have the impermeability expected if this operation is not successful.
6. A dry waste or some of its components having a specific gravity lower than SPC will float above the molten SPC, and as a result, and the waste form will be difficult to produce [7]. If the mixture remains molten for too long (e.g., 5 h in ref. 5), segregation between SPC and the incorporated waste may occur [5].
7. Only a very limited number of waste streams have, at this point, been tested with SPC. Four waste streams were studied by BNL (see Tables 4 and 5). Van Dalen and Rijpkema studied borate waste (a simulation of a pressurized-water reactor evaporator), lead iodide, a sludge resulting from water treatment, incinerator ash produced from burning a simulation of low level wastes, and ion-exchange resins [10] [21]. Their list of preferred

waste types for the encapsulation in an SPC matrix includes inorganic low- solubility compounds like sludges, precipitates, and incinerator ashes. According to these researchers, organic materials (because they do not adhere to SPC), ion exchangers (because they destroy the matrix by swelling pressure), and highly soluble compounds (because they capture water by osmotic pressure and provoke cracks of the waste form) are not good candidates. Kertesz et al. used SPC for the immobilization of incinerator ashes [13].

### 3.2.3 Durability of SPC Waste Forms

In the field of immobilization of low-level radioactive or mixed waste, durability issues include compatibility with other wastes and necessary conditions for disposal, extended immersion tests, maximum waste loading, effects of ion-exchange resins, biodegradation under environmental conditions, long-term waste form integrity, potential microcracking of large monolith surfaces on cooling, and possible inadequacy of existing NRC tests for biodegradation stability. These are discussed as follows:

1. Because SPC is not compatible with all waste species, the conditions for disposal must be studied prior to long-term or permanent storage (see Subsect. 3.2.2).
2. As a relatively new material, SPC's long-term durability has not been proven, even though some materials have been found to resist a highly corrosive environment for over 9 years (Table 3) [4]. In the field of immobilization of low-level radioactive or mixed waste, this process is still in the development stage [3]; therefore, no data exist on its long-term durability despite predictions by some that the durability of SPC could be twice that of PC [3].
3. Tests performed at BNL on the INEL incinerator ash containing 36 wt % zinc (primarily as zinc chloride) resulted in cracking and destruction of the waste form because of swelling of the dried salts when the waste form was immersed in water [5]. The addition of 0.5 wt % glass fibers was the solution found by the researchers to resolve the problem, at least over the 90-day duration of the test. Because of this observed

degradation problem, it would be very prudent to extend the length of regulatory immersion tests to well beyond 90 days when working with this type of matrix.

4. When testing SPC to determine the maximum waste loading this matrix can accept, BNL researchers observed during the immersion test in water a spalling of those waste forms containing very high salt loadings. The salt crystals present at the surface of the waste form were able to react with water; the swelling following this hydration provoked cracks that resulted in destruction of the waste form [1]. They especially observed this problem with sodium sulfate waste: at a waste loading of 50%, cracks appeared on the waste form surface after 48 days of immersion in water. However, Arnold et al. [3] stated that at the recommended value of 40% sodium sulfate, the waste form showed no sign of cracking, but again, note that the duration for the immersion test was only 90 days. The same problem was observed with boric acid waste at a waste loading of 57%, for the waste form exhibited severe cracking within only several days. One can expect then that such a phenomenon may occur with other anhydrous waste species if the waste loading is too high (i.e., if the particulates are too close to the surface of the waste form, where they can react with water from the environment).
5. Also, during preliminary tests BNL researchers observed spalling with waste forms containing ion-exchange resins. These waste forms were stored only in laboratory air with 20 to 25% relative humidity [1].
6. The resistance of elemental sulfur to biodegradation attack has not been proven, and some researchers have some concerns about the long-term durability of this material [22][19] (see Subsect. 3.1.5 ) in shallow land burials. Van Dalen and Rijkema state that biodegradation under environmental conditions is unknown [10].
7. Considering that little data have been published about the long-term durability of SPC waste forms, other than that covering the 90 days of the immersion test required by the NRC, one can be concerned about long-term waste form integrity, considering that a minimum 300-year storage period is required for low-level waste. The rationale at the foundation of this statement is based upon the following:

- a. Biodegradation tests performed following the NRC requirements do not employ conditions needed for bacterial growth on sulfur and are likely different than those for portland cement. Portland cement produces an alkaline environment created by the material and does not easily support the growth of most types of bacteria,
  - b. Ninety-day immersion tests have been shown to be too short in many instances for some cement-based waste forms; degradation may occur after a longer period of time. As an example, in the case of sulfate-containing waste streams, the mechanisms of degradation of the cement-based waste form will most often take more than 90 days. Therefore, one can also suspect that such phenomena can occur for SPC waste forms.
  - c. Elemental sulfur is not found on or near the surface of the earth, for it exists in a very narrow thermodynamic stability field. The stability field diagram for the sulfur-water system in Fig. 1 shows the very narrow stability field for elemental sulfur: it is not present above pH 8 and Eh measurements between 0 and 1 V. The diagram shows that sulfate would be a more stable form in most soil environments in the presence of oxygen, not elemental sulfur. For this reason, elemental sulfur is not found on the surface of the earth but well below it, where it is removed using high-pressure, 180°C steam employing the Frasch process. Large domes composed of gypsum, dolomite, and limestone protect the natural sulfur at depth from reacting chemically in places such as Louisiana, Texas, and Sicily. In the presence of oxygen and water, and above a pH of 8, sulfur is slowly oxidized to sulfate, especially when catalyzed by bacterial activity—a fact well known to gardeners and farmers who use elemental sulfur.
8. Because sulfur exists in different allotropic forms and has different densities that are sensitive to cooling rates, one may expect microcracking of the surfaces of large monoliths on cooling. Such stress cracks, pores, or other surface imperfections are excellent areas for oxidation and formation of expansive sulfate inside the cracks, resulting in further cracking and spalled surfaces. The smaller, high-surface-area pieces formed are then available for reaction with various types of indigenous, thiophilic soil bacteria. A schematic representation of this very plausible scenario is presented in Fig. 2.

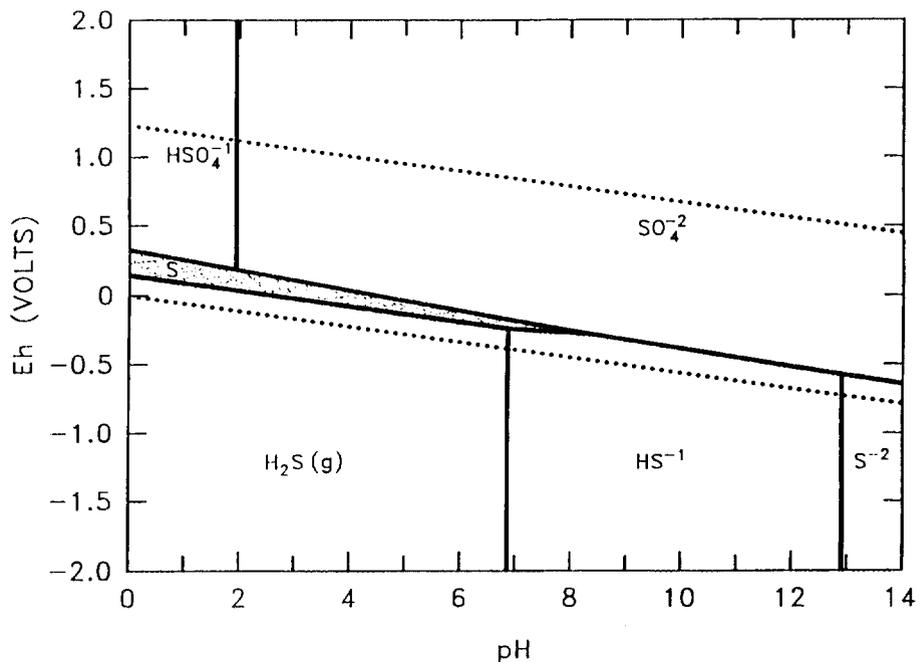
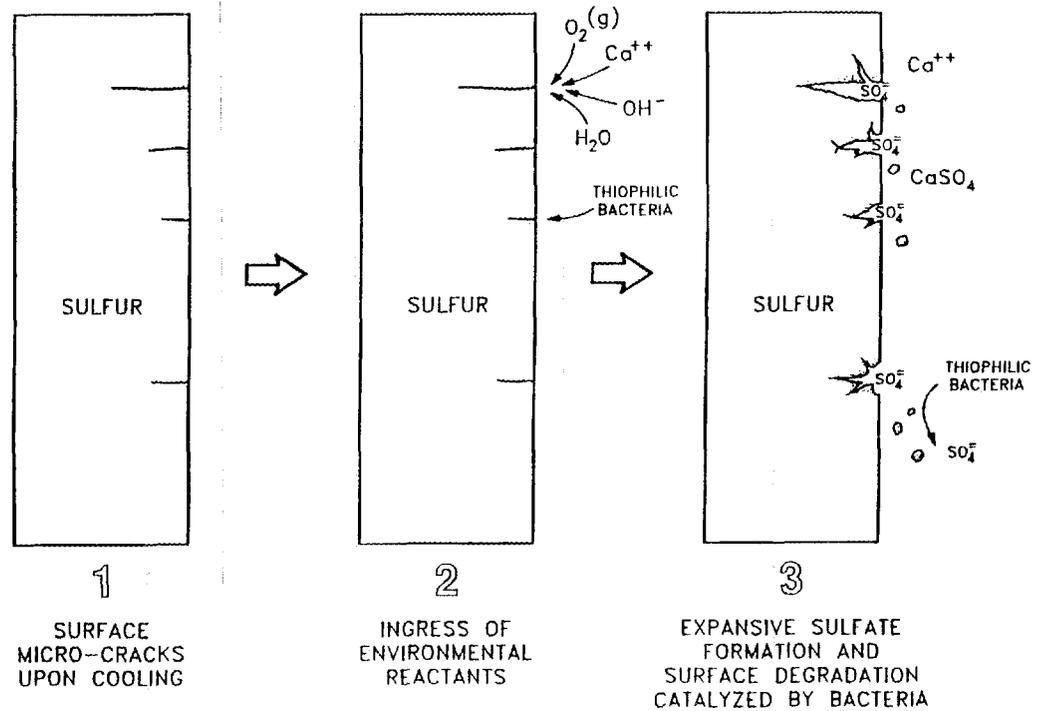


Fig. 1. Stability field diagram for the S-H<sub>2</sub>O System at 25°C.

The rate of this reaction to form sulfate in association with soil cations such as calcium or magnesium is very likely slow and dependent upon the ingress of oxygen or some other electron acceptor. For this reason, current regulatory short-term tests with nonthiophilic bacteria may not be adequate for SPC testing.

9. Torma [22] of INEL states that many studies on the degradation of elemental sulfur have been performed. In a conference held in August 1993 on biohydrometallurgical technologies, several publications discuss this topic [18][19]. Torma reported that possible biodegradation of elemental sulfur could jeopardize the durability of sulfur-based waste forms; therefore, this material might not be as safe as the current literature implies.



**Fig. 2. Schematic representation of elemental sulfur degradation due to sulfate formation and bacterial activity.**

Several publications discuss the action of *Thiobacillus ferrooxidans*, a chemolithotrophic bacterium capable of using sulfur and sulfur compounds as its source of energy, in the proceedings of a biohydrometallurgical technological symposium. The bacteria are able to oxidize elemental sulfur to sulfate over a broad pH range [18][19]. In the same proceedings other publications discussed other types of bacteria such as *Thiobacillus thiooxidans*, which are acidophilic and grow on elemental sulfur. Therefore, the existing NRC tests for biodegradation stability are likely not well suited for this new material; as a result, the lack of growth observed during the tests does not prove that biodegradation cannot occur for SPC.

A chemical reaction expected to occur during oxidative degradation by bacterial activity can be written as follows:



then



Elemental sulfur is oxidized to sulfite and then to sulfate by the sulfur- and sulfite-oxidizing enzyme systems [18][19] presented in Eqs. 1 and 2 above.

### 3.2.4 Operational Disadvantages

Operational disadvantages of SPC include the following:

1. An off-gas treatment system is needed to scrub vapors and gas released during mixing operations.
2. Handling, mixing, and use of SPC is more delicate than for PC (see Subsect. 3.1.6). Also, the control of the cooling phase is important because excessive voids can form that may be interconnected and thus jeopardize the impermeability of the waste form [3][4]. Computerized controls are necessary to maintain all the parameters at the optimum level (see Subsect. 3.1.6) and the temperature in a narrow operational window of  $\pm 10^\circ\text{C}$ .
3. The mixing equipment is more complex than for a standard PC mixer: the bowl and paddle both have to be heated, and a vacuum should be applied during mixing to facilitate removal of residual moisture and gases [23]. The mold receiving the molten mixture and its contents must be heated prior to and during the processing to control the cooling rate (see Subsect. 3.1.6) [5].

### 3.2.5 Safety Considerations

Safety-related issues are associated with this process. Molten SPC adheres to the skin on

contact and is generally more dangerous to handle and manipulate than PC [20]. Also present is a risk of forming toxic sulfur dioxide ( $\text{SO}_2$ ) and/or hydrogen sulfide gas ( $\text{H}_2\text{S}$ ), which are poisonous and flammable (see Subsect. 3.2.1). With good engineering control, however, these gaseous emissions should not be a problem; SPC is already used for commercial purposes, and such potential problems appear to be controllable.

### **3.2.6 Cost Considerations**

The cost for the SPC raw material is three times more than for portland cement [24]. The cost for producing an SPC waste form could be much higher than that for a PC matrix depending on the type of waste considered. The pretreatment step of drying the waste might be the most costly, especially if the waste has to be dried to contain less than 1% water. Also, more sophisticated equipment is necessary to prepare SPC waste forms. No data are available at this point on costs (including those for drying) for producing waste forms from real waste streams.

#### 4. CONCLUSIONS

By examining the advantages and disadvantages of the relatively new material SPC, as described in the literature, one realizes that this encapsulation process is not the answer to treating all waste streams. Even though this material presents some very interesting properties such as low porosity, low permeability, and impervious nature to water, there are limits to the use of SPC as a matrix for immobilization of wastes—just as there are limits for other processes such as portland cement, bitumen, glass, or organic binders.

As a new material, this process might need more comprehensive testing over longer periods of time than reported in the published results to date, especially when low-level radioactive or mixed wastes are immobilized. No results were found on the durability of SPC after 90 days for waste forms produced with low-level radioactive or mixed wastes. Considering the very narrow thermodynamic stability field of elemental sulfur, this issue could become a major concern when considering the minimum 300-year storage period for such waste forms. The catalyzed degradation of elemental sulfur by microorganisms could also become an important issue and must be addressed if SPC is to see commercialization.

Preliminary full-scale tests performed by INEL indicate that (1) this material still requires a lot of precautions for the safe production of quality waste forms and (2) further engineering issues must be solved before the process can be operational. One major limitation associated with the use of this matrix may be the moisture content of the waste. The cost of achieving a moisture content of less than 1% may become very prohibitive for slurries or wastes containing large amounts of water. Using this material as the last stage following the process of incineration of wastes could be a good use for such a medium since the ashes will be nearly free of water.

Long-term durability of the SPC waste form must be studied further. The treatability study performed at INEL is a good example and shows that some waste streams are better suited for one matrix than another. Table 7 presents the summarized advantages and disadvantages of SPC and PC processes.

**Table 7. Sulfur polymer cement and portland cement:  
advantages and disadvantages**

Advantages	Disadvantages
<b>Portland cement</b>	
<ul style="list-style-type: none"> <li>• Low cost</li> <li>• Proven stability in most cases</li> <li>• Safer ingredients</li> <li>• Simple equipment</li> <li>• Variety of formulations available</li> <li>• Low concentrations of some organics can be treated</li> <li>• Suited for wet wastes</li> <li>• By tailoring formulations, most of the disadvantages can be eliminated or greatly reduced (e.g., free liquid, heat of hydration, and porosity)</li> <li>• Effectiveness proven for the stabilization/immobilization of many radioactive and hazardous species</li> </ul>	<ul style="list-style-type: none"> <li>• Volume and mass increase of the waste form</li> <li>• Not well suited for wastes having high concentrations of salts and organics</li> <li>• Higher permeability</li> <li>• Heat of hydration can be a problem</li> <li>• Possibility of free-standing liquid</li> <li>• Inhibitor species can alter or prevent the set</li> <li>• Chemical characterization of the waste more demanding</li> <li>• Risk of gas generation during irradiation</li> </ul>
<b>Sulfur polymer cement</b>	
<ul style="list-style-type: none"> <li>• Chemical characterization of the waste less demanding</li> <li>• Impermeability</li> <li>• Fast hardening and high strength obtained</li> <li>• Higher waste loading</li> <li>• Resistant to many chemicals</li> <li>• No need for rinse of equipment; longer time window for using the material</li> <li>• Biodegradation by bacteria not observed during the NRC test, but elemental sulfur can be oxidized by bacteria</li> <li>• NRC tests successful for some waste streams studied</li> <li>• No generation of gas during the irradiation test</li> <li>• No free-standing liquid</li> <li>• Immobilization of toxic metals was successful with some waste streams</li> <li>• Low leachability for radionuclides</li> <li>• No long-term performance available</li> <li>• Higher cost</li> <li>• More complex engineering equipment and operations.</li> </ul>	<ul style="list-style-type: none"> <li>• All waste streams must be dried (0 to &lt;1% water); not well suited for wet wastes</li> <li>• Waste should be heated at least to 200°C prior to incorporation in SPC</li> <li>• Not well suited for some wastes; alkalis &gt; 10%, oxidizers, nitrate salts, organics, ion exchangers, and highly soluble compounds</li> <li>• Safety equipment necessary to control the process and to prevent H<sub>2</sub>S and/or SO<sub>2</sub> emission</li> <li>• Off-gas system</li> <li>• Waste form could be deformed for temperatures &gt;88°C</li> <li>• Disposal restrictions</li> <li>• Waste form can burn</li> <li>• Wastes with densities below SPC density will float above the molten material</li> <li>• Limited number of waste streams tested, limited history.</li> </ul>

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