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SULFUR POLYMER CEMENT,  
A SOLIDIFICATION AND STABILIZATION AGENT  
FOR HAZARDOUS AND RADIOACTIVE WASTES

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## ABSTRACT

Hydraulic cements have been the primary radioactive waste stabilization agents in the United States for 50 years. Twelve years ago, Brookhaven National Laboratory was funded by the Department of Energy's Defense Low-Level Waste Management Program to test and develop sulfur polymer cement (SPC). It has stabilized routine wastes as well as some troublesome wastes with high waste-to-agent ratios. The Department of Energy's Hazardous Waste Remedial Action Program joined the effort by providing funding for testing and developing sulfur polymer cement as a hazardous-waste stabilization agent. Sulfur polymer cement has passed all the laboratory scale tests required by the U.S. Environmental Protection Agency and U.S. Nuclear Regulatory Commission. Two decades of tests by the U.S. Bureau of Mines and private concrete contractors indicate this agent is likely to exceed other agents in longevity. This bulletin provides technical data from pertinent tests conducted by these various entities.

## ACRONYMS AND TERMS

Since the latter 1800s, the generic terms "sulfur cement" and "sulfur concrete" have appeared in hundreds of technical reports on elemental sulfur combined with various experimental additives. Many reports cite failures that we could not tolerate in the treatment of radioactive wastes--none of those reports are relevant to the topic of this paper. Unfortunately for today's researcher, authors reporting on "sulfur polymer cement," which is the topic of this paper, also often used the same generic terms "sulfur cement" and "sulfur concrete" for the sole purpose of brevity; therefore, the researcher could easily become confused. The correct terms for the substances addressed in this paper are "modified sulfur cement" and "sulfur polymer cement." These terms are synonymous and for clarity are given the acronym "SPC." An additional tip to the researcher is that SPC was not developed until 1972.

It is also necessary to identify an acronym for "sulfur polymer cement concrete," which is "SC." The reader needs to understand that once the aggregate/waste is added to SPC (the cement), it becomes SC (the concrete), whether the mass of either substance is liquefied or solid. Hereafter, the words "cement" and "concrete" refer to the generic family of hydraulic cements and concretes, while "PCC" refers to the specific hydraulic cement concrete known as portland cement concrete.

The terms "solidification" and "stabilization" are essentially synonymous in many regulatory documents;<sup>1</sup> however, solidification here means conversion of a fluid mass to a solid, while "stabilization" means preventing the solidified waste from interacting unfavorably with the environment for specified periods of time.

## INTRODUCTION

The U.S. Congress attacked the environmental problem of hazardous waste disposal, and thus mixed waste (MW) disposal, by pressing for permanent solutions for waste treatment rather than continued remediation through an evolution of laws. The need for a waste stabilization program was defined in the Resource Conservation and Recovery Act (RCRA), the Comprehensive

Environmental Response, Compensation, and Liability Act (ERCLA), the Hazardous and Solid Waste Amendments (HSWA), and the Superfund Amendments Reauthorization Act (SARA).<sup>1</sup>

The government's goals are to decrease the surface to mass ratio, thereby reducing the potential surface area exposed to sulfates that attack the concrete; to improve the handling characteristics; to improve the physical characteristics by reducing permeability and leachability; and to further reduce solubility of hazardous components by adjusting the pH.<sup>2</sup>

Within the Department of Energy (DOE) system, sclerification and stabilization agents for low-level radioactive wastes (LLW), and MWs were failing to pass governmental tests at unacceptable rates, or were passing the tests with very low waste-to-agent ratios. Recognizing that problem at the beginning of the 1980s, the DOE's Defense Low-Level Waste Management Program sought other potential waste sclerification and stabilization agents that might supplement or replace concrete.

The development and testing of SPC by the U.S. Bureau of Mines, and the tests conducted by universities, states, and by the concrete industry during the past two decades were very promising. The ability of SC to withstand acid, salt, and sulfate attacks that destroyed concrete offered strong evidence that SPC might perform better in stabilizing the waste than concrete. However, tests by DOE were necessary to determine if SPC would accommodate reasonable loadings of radioactively contaminated wastes and still provide adequate stabilization.

Since stabilization is the primary goal in waste disposal, DOE's Defense Low-Level Waste Management Program funded research and testing of SPC laden with LLW at Brookhaven National Laboratory throughout most of the 1980s. DOE's Hazardous Waste Remedial Action Program (HAZWRAP) added funding in recent years towards testing hazardous and mixed wastes in SPC. This paper summarizes those tests.

Pertinent data provided by commercial tests of SPC and SC are vital to understanding the potential of SPC for stabilization of LLW, MW, and hazardous

wastes. Therefore, those data are also included in this paper, and are presented first.

## DEVELOPING AND TESTING SPC AND SC FOR HARSH CHEMICAL ENVIRONS

### Developmental Background

Pollution abatement efforts during the past 30 years produced sulfur through petroleum refining, natural gas processing, and recovery from geothermal power plants. The construction industry had been plagued with billions of dollars of concrete failures caused by salt and acidic attack in highway bridges, fertilizer plants, metallurgical applications, and chemical processing facilities to name a few. Those failures provided the Bureau of Mines with a potential use for sulfur--a better concrete.

Elemental sulfur has been used as a cement since prehistoric times, but it lacked mechanical strength and durability and it shrank too much. All of these problems were caused by changes in the crystalline structure during cooling. The Bureau of Mines discovered in 1972 that the addition of dicyclopentadiene and oligomers of cyclopentadiene in equal quantities totaling 5wt% of the sulfur phase resulted in an excellent construction concrete having advantageous properties not found in other concretes.<sup>2,3</sup> The U.S. Bureau of Mines and The Sulphur Institute joined forces in an effort to find useful construction purposes for the nation's increasing stockpiles of sulfur. In 1973 the Sulphur Development Institute of Canada joined the effort.<sup>4</sup>

### Properties of SPC and SC

The various mechanical strengths of SC are approximately double those of PCC and are not specifically cited herein; however, they are detailed in Reference 5. While it takes the average PCC approximately 28 days to achieve a compressive strength of 4000 psi, SC reaches that strength upon cooling and continues to gain strength for approximately one month.<sup>2</sup>

Impermeability of waste stabilization agents is desirable for environmental enhancement efforts;<sup>1</sup> therefore, the following finding was most important if it

can be duplicated with MW and LLW. "Static water-permeation tests were made to compare the permeability of SC and PCC. Five-foot sections of 6-in. diameter plastic pipe were bonded to the surface of 2-in thick slabs of SC and PCC. A 51-in. column of water was placed in each pipe section to provide a 1.84 psi water pressure on the surface of the slabs. The SC showed no loss in water height after 6 months, while the PCC slab showed more than a 1-in./h loss of water height by permeation through the more porous PCC material. There was no penetration of water through the SC slab."<sup>2</sup> The explanation of these test results comes from the physical properties of the two substances; while they both have approximately the same volume of pores (void space), the pores in SC are not connected, whereas the pores in concrete are.<sup>2, 6</sup>

In the early 1970s, the Bureau of Mines worked with the U.S. Environmental Protection Agency (EPA) to protect miners from radon gas. A spraying concept was developed and patented that applied a 1/4-in.-thick lining of SC on mine walls, which prevented the entrance of radon gas.<sup>7</sup> This effort showed SC to be impermeable to radon gas as well as water.

The impermeability of properly prepared SC is well established. However, if the SC is cooled too quickly, it will contain an excess of voids that will connect with each other; if the aggregate in the SC contains water, tiny steam vents will develop; or if the wrong aggregate is used, the SC will become porous. Any of these events will allow both water and gas to penetrate the solidified SC. Since it is possible that these conditions could occur with improper mixing, it is safer to say that construction-grade SC is "virtually impermeable," or "can be made impermeable" to water and to gas.

SC made with construction aggregate and SPC are both nontoxic.<sup>8</sup> Sulfates attack PCC, but have little or no effect on the integrity of SC.<sup>2, 4</sup> SC is corrosion-resistant, and its impermeability protects steel reinforcing materials (and metal waste) from oxidation and subsequent concrete rupture. Where strength and fracture resistance are primary goals, glass fibers, synthetic fibers, epoxy-coated rebar, steel rebar, or a combination thereof can be added.<sup>5, 9</sup> SC is nonreactive with steel. Where controlled shrinkage, minimization of cracks, ductility, and impact resistance are needed, glass fibers are added.<sup>6</sup> Shrinkage, on the average, is 0.1%, slightly greater than

PCC.<sup>5, 9</sup> SC is resistant to damage by freeze-thaw cycling, and has coefficients of expansion compatible with those of other construction materials such as concrete and reinforcing steel. Creep is roughly half that of PCC.<sup>9, 10</sup> Where SC and PCC are made with the same aggregate, their densities are the same, 150 lb/ft<sup>2</sup> on the average.<sup>4</sup> Viscosity of SPC is approximately 50 cp at 135°C (275°F),<sup>4</sup> which approximates the viscosity of automobile engine oil. The addition of aggregate to SPC converts it to SC, and as more aggregate is added the viscosity increases.

As a thermoplastic, SC will melt every time its temperature is elevated to 110°C (230°F); however, its poor thermal conductivity (0.2 - 0.5 BTU/h ft °F) is a strong deterrent to melting. When heat is removed, the SC will regain its original strength very rapidly. Because SC is a thermoplastic, its mechanical properties are affected by sustained high temperature--its highest operational temperature is 88°C (190°F)<sup>5</sup>.

#### Tests of SC in Successful Applications

SC is a durable, high-strength concrete that is resistant to abrasion and to attack by most acids and salts. It is best used where exposed to high concentrations of mineral acids, corrosive electrolytes, salt solutions, or corrosive atmospheres in general.<sup>4, 5, 9</sup> SC has high potential in chemical, metallurgical, and fertilizer applications.<sup>2</sup> (These properties suggested longevity in SC that concretes did not exhibit, and thus SC was a strong candidate for waste stabilization.)

A sampling of reported test results illustrates SC's resistance to attack by adverse chemicals that routinely attack concrete. After being exposed to sulfuric acid solutions and copper electrolytic solutions for nine years, SC showed no evidence of corrosion or deterioration.<sup>3</sup> In a six-year test in a chemical processing plant, PCC was attacked and completely destroyed in some cases, while SC showed practically no evidence of strength loss or material degradation.<sup>8</sup> After seven years of exposure to a salt environment in a test in a potash chemical storage building, two SC structural support piers were undamaged, while the PCC pier in the same location was heavily damaged after only two and a half years.<sup>9</sup>

### Tests of SC in Unsuccessful Applications

In contrast, SC has been shown to deteriorate in hot concentrated chromic acid solutions, hot organic solvent solutions, sodium chlorate-hyperchlorite copper slimes, and strong alkali (over 10%). SC is not recommended in areas handling strong bases, strong oxidizing agents, aromatic or chlorinated hydrocarbons, or oxygenated solvents.<sup>4, 6</sup>

### Regulating the SPC Industry

In 1990, the American Society for Testing and Materials (ASTM) issued the specification for SPC entitled: Standard Specification for Sulfur Polymer Cement for Use in Chemical-Resistant, Rigid Sulfur Concrete, Designation: C1159-90.

### TESTING AND MODIFYING SPC FOR SOLIDIFICATION AND STABILIZATION OF WASTES

As indicated in the preceding section, the commercial tests of SPC and SC showed potential for both solidification and stabilization of hazardous and radioactive wastes. Therefore, at the beginning of the 1980s, the DOE's Defense Low-Level Waste Management Program funded the Waste Management Research and Development Group at Brookhaven National Laboratory (BNL) to research, develop, and test potential LLW stabilization agents. The research was to meet the intentions of governmental laws by minimizing costs and radiation exposure to operators, while providing environmental enhancements that would ensure public safety.<sup>11</sup> That effort has continued. DOE's HAZWRAP has provided the more recent funding of tests, which were directed toward stabilizing MW and passing the EPA and NRC tests, which would allow disposal in LLW disposal sites rather than in very expensive MW disposal sites. Likewise, stabilization of hazardous wastes would allow disposal in non RCRA disposed sites.

After evaluating potential agents, two thermoplastics, SPC and low-density polyethylene, were selected for further development and testing against EPA and NRC testing standards.<sup>11</sup> PCC was selected as the comparison standard and was tested using the same waste components each time SC and polyethylene were tested. This section discusses those efforts.

## The Chemistry of Solidification

Some radioactive wastes once thought to be stabilized in concrete were not. Whether or not concrete hardens depends on the chemical hydration reaction dictated by both the chemistry and the amounts of water, cement, waste, plasticizers, and other additives. In other words, elements in the waste and the binder itself often cause an interaction that can retard or prevent solidification.<sup>12, 13</sup>

Because SPC is a thermoplastic, it requires no chemical reaction for solidification. Therefore, normal precautions in temperature control, pretreatment of the waste, and assurance that the waste is compatible with SPC will ensure that the SC will always solidify when it cools below the melt point. SPC will accept a wide range of wastes (aggregate) with divergent chemical and physical compositions. SPC is easier use than other thermoplastics, like polyethylene, because of SPC's low viscosity and low-melt temperature.<sup>2, 12</sup>

Incinerators reduce organic waste volume by as much as 300 times. Therefore, the resultant fly ash contains highly concentrated remnants of the original waste. Heavy metals in the waste that originally fell short of the EPA definition of hazardous waste are likely to be elevated to the hazardous zone. The curie count per unit volume of LLW is also raised, so the ash is still radioactive, and assuming the waste is raised to the hazardous level, the ash is classified as MW and will not pass EPA's Toxicity Characteristic Leaching Procedure (TCLP) test without further treatment. Before this ash can be disposed of in LLW disposal facilities, it must be treated sufficiently to pass the TCLP test.<sup>10</sup>

## Tests Completed to EPA Standards

MW fly ash was obtained from the Waste Experimental Reduction Facility (WERF) located at DOE's Idaho National Engineering Laboratory (INEL). The MW contained the following components (expressed in weight percentages): zinc 36, lead 7.5, sodium 5.5, potassium 2.8, calcium 0.8, copper 0.7, iron 0.5, and cadmium 0.2.<sup>10</sup> The EPA considers both lead (Pb) and cadmium (Cd) to be toxic

metals. The ash also contained highly soluble metal chloride salts (primarily zinc chloride) that increase the mobility of contaminants while interfering with the solidification reaction of conventional solidification and stabilization agents. The fly ash was combined with SPC and was tested to the EPA's Extraction Procedure Toxicity (EP Tox) test,<sup>14</sup> and the TCLP test.<sup>15</sup> Both Cd and Pb were still above the concentration limits allowed under RCRA, so additives were sought that would further reduce the mobility of the toxic metals. Sodium sulfide (Na<sub>2</sub>S), which reacts preferentially with Cd and Pb to form highly insoluble metal sulfides, was selected. By adding 7wt% Na<sub>2</sub>S to 50wt% SPC and mixing it with 43wt% MW fly ash, the resultant concrete passed the EPA's TCLP test, thus allowing disposal as non-RCRA waste.<sup>10,12</sup>

SPC has proven effective in reducing the leach rates of reactive heavy metals to the extent that some MW can be managed as solely LLW. When SPC is combined with mercury and lead oxides (both toxic metals), they interact chemically and form mercury sulfide (HgS) and lead sulfide (PbS), both of which are insoluble in water.<sup>10, 16</sup> Because it is the hazardous waste components rather than the radioactive components that hinder solidification, the following discoveries are important. The California State Department of Health Services used a dried residue sulfur from petroleum refining that contained 600 leachable ppm vanadium (a carcinogen) to manufacture SPC and thereby reduced the leachable vanadium to 8.3 ppm. That was well below the soluble threshold limit concentration of 24 ppm established by the State of California, and thus permitted disposal in a sanitary landfill.<sup>16</sup>

The Northern California Power Authority, Middletown, California, extracts considerable quantities of sulfur from its geothermal power Stretford H<sub>2</sub>S Abatement Facility. They recover elemental sulfur in sulfur cake, which is a 50:50 mixture of sulfur and water with trace heavy metals, vanadium, mercury, and arsenic. Cost is high for its disposal in an EPA-approved disposal site. In a joint environmental-enhancement and cost-saving venture, they are designing a facility to produce high-quality SPC from the waste sulfur and its hazardous contents, thereby creating a SPC that will pass the EPA tests and can thus be disposed of in sanitary land fills or be sold as a solidification and

stabilization agent for LLW and MW treatment and disposal. They plan start-up in 1992.<sup>a</sup>

Tests Completed to NRC Standards

The NRC has established a qualifier list of tests under the title "Waste Form Qualification Testing."<sup>17</sup> Where possible, the tests are to the standards of the ASTM, American National Standards Institute (ANSI), and American Nuclear Society (ANS). The tests are: (a) general (guidelines that apply to the conduct of the remaining tests); (b) compression (lower limit recently raised from 60 psi to 500 psi); (c) thermal cycling (30 cycles of temperature change from -40 to 60°C); (d) irradiation (exposure to a minimum dose of 10E+8 Rad); (e) biodegradation (test susceptibility to fungi and bacteria); (f) leach testing (immersion in water for 90 days followed by leachate analysis); (g) immersion testing (check for 500 psi compressive strength following immersion in water); (h) freestanding liquids (check for lower limit of 0.5 vol% liquids); and (i) full-scale testing (pour full-scale monolith followed by tests b and g above).

After the immersion test was completed, compressive strengths of waste-impregnated SC ranged from a low of 1998 psi for 40wt% boric acid, to a high of 6435 psi for 40wt% incinerator ash, with sodium sulfate falling in between. Compressive strength tests after freeze-thaw cycling found some increase and some decrease in strength with different wastes--these were of no consequence in reference to the NRC requirement of >500 psi.<sup>2</sup>

When the leach tests were completed, the leach rate was found to be lower for incinerator hearth ash than for highly soluble sulfate salts. The leach rate was four to eight orders of magnitude less than the leach index established by the NRC. The conclusion was that radionuclides leach slowly in SC.<sup>12</sup>

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<sup>a</sup>Confirmed in telecommunication with Mr. Murry Grande, Northern California Power Authority, September 5, 1991.

The NRC tests for biodegradation of SC were completed successfully with "no growth" being the result of both the ASTM G-21 and ASTM G-22 tests. The NRC irradiation test to 10E+8 Rad was completed successfully.<sup>18</sup> Initially some deterioration was detected in the SC and mixed waste fly ash combination when subjected to the immersion test, but that problem was corrected by the addition of 0.5wt% glass fibers, an additive recommended by the Bureau of Mines for strengthening SC.<sup>5, 6, 18</sup>

Research and development resulted in a modified SPC that can now stabilize waste types like dehydrated boric acid salts, incinerator hearth ash, MW fly ash, and dehydrated sodium sulfate salts that have heretofore defied solidification and stabilization in concrete in any significant quantity. Many of the extensive efforts at testing the waste and developing a formula of hydraulic cement, water, and various additives to match the waste chemistry can be eliminated. The modified SPC offers a monolithic waste form that is durable in harsh environments.<sup>12</sup>

#### Comparison of Waste-to-Agent Ratios

Comparative test results show that a given quantity of waste requires less SPC than PCC to achieve a stabilized waste form that will satisfy EPA and NRC requirements. The following numerical advantages of SPC over PCC were calculated: 6.7 times less SPC with sodium sulfate, 3.8 times less SPC with boric acid, 1.1 times less SPC with incinerator bottom ash, and 4 times less SPC with incinerator fly ash.<sup>12</sup> The average was 3.9 times less SPC than PCC.

#### One Test to NRC Standards Remains

The NRC's final test, the full-scale test, is required in order to give SPC full credibility as a waste solidification and stabilization agent. With all the laboratory tests completed, a full-scale test demonstration is planned.<sup>12</sup>

A successful test pour of SPC laden with 43wt% industrial incinerator fly ash was completed in a 1m x 1m x 1m wooden box containing simulated contaminated scrap metals. Tests of full-scale SPC mixers have been and are being conducted in an effort to select one that can be used for the full-scale

tests and continue afterwards as an operational SPC mixer.<sup>19, 20</sup> High on the desirability list is a mixer with a large heated surface area in the mixer blades and shaft as well as in the jacket surrounding the mixer for firm control of internal heat. Another priority is to use a weir (dam) rather than a valve to avoid flow-control problems normally associated with valves used in concreting operations.<sup>21, 22</sup>

#### Wastes That Cannot be Combined with SPC for Stabilization

Many common waste streams cannot be solidified in SC in their original condition. The combining of sodium nitrate salts with SPC is not recommended because the two compounds, when combined, could cause a "potentially reactive mixture."<sup>12</sup> Another rejection is ion-exchange resins. SC is weakened dramatically by wet aggregate (waste), but it was assumed that ion-exchange resins could be dried and solidified in SC. However, that effort proved futile. Ion-exchange resins will take on any available water where the resins are exposed at the surface, and will swell and gradually rupture SC.<sup>2</sup> Early commercial tests showed that expanding clays could not be used in SC for the same reason.<sup>4, 6</sup> Other wastes, like sludges, evaporator bottoms, absorbed liquids, biological waste, animal carcasses, and even dirt must first be treated to a dry condition before being solidified in SC.

The need for incineration or vitrification of those troublesome wet wastes before introduction to any solidification agent has long been recognized in the nuclear industry.<sup>1</sup> Once reduced to ash or glass, many wastes stand an excellent chance of passing the required NRC and EPA tests when solidified in SC.<sup>23</sup>

#### SAFETY AND ALARA CONSIDERATIONS

"Sulfur is the chemical industry's most widely used raw material";<sup>24</sup> therefore a great deal of information is available on handling it safely. A safe working environment is ensured by following the appropriate procedures provided by the National Safety Council,<sup>24, 25</sup> National Fire Protection Association,<sup>26</sup> U.S. Department of Health and Human Services,<sup>27</sup> National

Institute for Occupational Safety and Health,<sup>27</sup> National Institute for Occupational Safety and Health,<sup>27</sup> and the Manufacturing Chemists' Association, Inc.<sup>28</sup>

SPC is procured in pellet or granular form, which provides handling capabilities with minimum creation of dust. Airborne SPC dust can be explosive if all conditions are correct and normal safety precautions are not exercised. SPC/SC will also emit hydrogen sulfide gas to the off gas system if excessive temperatures are created--normal heat control systems with backup gas-detectors will prevent a safety hazard.<sup>24,25,26,27,28</sup>

The recommended mixing temperature for SC is 127 to 138°C (260 to 280°F), which will minimize gaseous emissions to the off-gas system and provide optimum viscosity. SC can be maintained in the recommended pouring-temperature range in a mixer for long periods of time, yet remain plastic and workable until placement.<sup>21, 23</sup>

SPC and SC will burn if held in a flame, but will self extinguish when the heat is withdrawn.<sup>3, 5</sup> The U.S. Department of Transportation (DOT) classifies materials for transportation and establishes flammability ratings for essentially all commodities. SPC and SC meet none of the DOT criteria for classification as flammable materials.

#### CONTINUED SPC TESTING

Irradiation tests were recently completed at Oregon State University (OSU). The original intent was to test lead-laden SC as a possible personnel shielding for high-radiation areas. Twelve SC specimens containing high loadings of lead oxide were subjected to 10E+8 Rad, as prescribed in the NRC irradiation test. The test specimens showed no visible signs of deterioration (no spalling, cracking, or other evidence of disintegration) and they exceeded NRC's requirement for 500 psi compressive strength.<sup>29</sup> In fact, the specimens actually gained significant compressive strength during the irradiation test, and were an order of magnitude better than NRC requirements. The physical and

mechanical characteristics of the test material before and after the test will be released in their final report.<sup>b</sup>

There were no radioactive wastes combined with the SC for the OSU test; however, it is the hazardous or chemical components rather than the radioactive components that cause problems in solidification. Lead is a toxic metal, a problematic hazardous waste, so this test was important in the evaluation of SPC as a viable stabilization agent.

Since NRC requires only 500 psi compressive strength, and since the SC, which contained various wastes, averaged approximately 4000 psi,<sup>2</sup> there is a large "window of opportunity" for experimentation to develop the optimum SC mixture for given waste forms. The principal developer of SPC and SC says the construction-grade SPC being used in the EPA and NRC tests for the past decade was never intended for that purpose. He is currently developing a "second generation SPC," which he believes will perform even better as a LLW and MW stabilization agent.<sup>c</sup>

Encouraged by the DOE experimentation, the Bureau of Mines, Division of Environmental Technology, began a new testing program for SPC and SC to seek treatment solutions to hazardous waste created in industrial incinerators and furnaces. The ultimate goal is removal of the ash from the hazardous classification. Towards accomplishing that goal, they will investigate the cross linking, the chemical bonding, between SPC and heavy metals, and determine if it is adequate to pass the TCLP test with heavy waste loadings. If not, they plan to seek new SPC formulations, or heat treatments, that will improve both situations.<sup>30, 31, 32</sup> Whatever they accomplish will be a benefit to DOE efforts in developing exemplary treatment and disposal of LLW and MW.

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<sup>b</sup>Test results confirmed in telecommunication with Mr. William C. McBee, the Irradiation Test Manager, June 4, 1991.

<sup>c</sup>Confirmed in telecommunication with Mr. William C. McBee, the primary developer of SPC, February 28, 1991.

## SUMMARY

Prime threats to adequately solidified and stabilized LLW and MW are water in the waste, lack of leach resistance, permeability, biodegradation, inability to withstand chemical attack both from within the solidified mass and from the disposal environment, and ultimately the inability to consistently meet EPA and NRC requirements for disposal. Two decades of tests in the commercial sector and a decade of tests in a DOE laboratory shows SPC to be better in most cases in those areas when compared to other tested solidification and stabilization agents. SC has passed all the required EPA and NRC laboratory tests. The NRC's full-scale test remains to be completed.

## CONCLUSIONS

Federal and State laws mandate ever increasing requirements for solidification and stabilization of LLW and MW. Solidification and stabilization agents used in the past for selected wastes were not passing the required tests at acceptable rates. SPC shows promise of being able to accommodate many of those wastes. Current laws encourage full treatment of wastes, and with incineration and/or vitrification of all candidate wastes, the potential for successful solidification and stabilization of many more waste streams using SPC is good.

The perfect waste solidification and stabilization agent has not yet been discovered. SPC will not accommodate all wastes. Tests to date show that SC can solidify a wide range of wastes, and will normally accommodate a higher waste loading than other agents. Sulfur is a stable element, and tests suggest that SPC is also stable. SPC may well be a stabilization agent that will preserve wastes well beyond the required time periods. Further testing will be required to verify this possibility.

## REFERENCES

1. U.S. Environmental Protection Agency, Stabilization/Solidification of CERCLA and RCRA Wastes, EPA/625/6-89/022, May 1989.
2. Kalb, P.D., P. Colombo, et al., Modified Sulfur Cements Solidification of Low-Level Wastes, BNL 51923, October 1985.
3. McBee W.C. and H.H. Weber, "Sulfur Polymer Cement Concrete," Summary and Proceedings, Twelfth Annual U.S. DOE Low-Level Waste Management Conference, Chicago, Illinois, August 28 & 29, 1990, CONF-9008119-Proc.
4. McBee, W.C., T.A. Sullivan, H.L. Fike, "Sulfur Construction Materials," Bulletin 678, U.S. Department of the Interior, Bureau of Mines, 1985.
5. National Chempruf Concrete, Inc., Chempruf Reference Document, Clarksville, Tennessee, October 1988.
6. Fowler, D.W. et al., "Guide for Mixing and Placing Sulfur Concrete in Construction," Report of ACI Committee 548 in the ACI Materials Journal, ACI 548.2R-88, Title no. 85-M36, July-August 1988.
7. Dale, J. M., and A. C. Ludwig, "Sulfur Coating for Mine Support" (contact H0210062, Southwest Res. Inst.), BuMines OFR 31-73, 1972, 46pp.: NTIS PB 220 408
8. Tox Monitor Laboratories, Inc., "Plasticized Sulfur 5% DCPD Oligomers," TM 82-356, 1983.
9. McBee, W.C. and D.J. Donahue, "Corrosion Resistant Concrete," McBee and Associates, Lebanon, Oregon.
10. Kalb, P.D., J.H. Heiser III, P. Colombo, "Encapsulation of Mixed Radioactive and Hazardous Waste Contaminated Incinerator Ash in Modified Sulfur Cement," BNL-43691.

11. Brookhaven National Laboratory, "Waste Form Development Program Annual Report, 1982
12. Kalb, P.D., J.H. Heiser III, P. Colombo, "Comparison of Modified Sulfur Cement and Hydraulic Cement for Encapsulation of Radioactive and Mixed Wastes," Summary and Proceedings, Twelfth Annual U.S. DOE Low-Level Waste Management Conference, Chicago, Illinois, August 28 & 29, 1990, CONF-9008119-Proc.
13. Darnell, G.R., personal communication to J.D. McKinney, EG&G Idaho, Inc., "Trip Report for ORNL's Workshop on Radioactive, Hazardous, and/or Mixed Waste Sludge Management," GRD-02-91.
14. U.S. Environmental Protection Agency, 40 CFR 261, Appendix II, EP Toxicity Test Procedures, 45 FR 33119, May 19, 1980, as amended by 48 FR 14293, April 1, 1983 and 50 FR 663, January 4, 1985, Washington, DC.
15. U.S. Environmental Protection Agency, 40 CFR 261, Appendix II-Toxicity Characteristic Leaching Procedure (TCLP), 55 FR 11863, March 29, 1990, Washington, DC.
16. Treatment Standards for Liquid Redox Waste in California, State of California Department of Health Services, Toxic Substances Control Program, Alternative Technology Division, June 1990.
17. U.S. Nuclear Regulatory Commission, "Technical Position On Waste Form," (Revision 1), Low-Level Waste Management Branch, Division of Low-Level Waste Management and Decommissioning, January 1991.
18. Kalb, P.D., J.H. Heiser III, R. Pietzak, P. Colombo, "Durability of Incinerator Ash Waste Encapsulated in Modified Sulfur Cement," BNL-45292

19. Aldrich, W.C., EG&G Idaho, Inc., personal communication to Mr. J.A. Logan, "Trip Report on Visits to F.E Ward Co. to Pour Sulphur Cement into a 1-Cu-Meter Form & Visit Lone Star Cement Co. to Observe Their Filtering System for Removing Suspended Cement From the Wash Water," WCA-7-90, September 25, 1990.
20. EG&G Idaho, Inc., "Test Plan, Pour Sulfur Polymer Cement into Steel Containers that are Partially Filled With Metal Objects," Work Package Number 35820GRT1, October 1, 1991.
21. Darnell, G.R., EG&G Idaho, Inc., personal communication to distribution, EG&G Idaho, Inc., "Trip Report for Hanford Technical Exchange, Sulfur Polymer Cement as a Waste Stabilization/solidification Agent," GRD-13-91, May 8, 1991.
22. Darnell, G.R., EG&G Idaho, Inc., personal communication to Mr. John Shade, Richland, Washington, "Request for Papers on Sulfur Polymer Cement/Concrete," GRD-33-90, December 14, 1990.
23. E. R. Johnson Associates, Inc., "An Assessment of the Potential of Modified Sulfur Cement for the Conditioning of Low-Level Radioactive Waste for Dumping At Sea," JAI-200, June 1983, prepared for Brookhaven National Laboratory, New York
24. National Safety Council, "Handling and Storage of Solid Sulfur," Chicago, Illinois, Data Sheet I-612-79, 1979.
25. National Safety Council, "Handling Liquid Sulfur," Chicago, Illinois, Data Sheet I-592 Rev. 83, 1983.
26. National Fire Protection Association, Inc., "Standard for Prevention of Sulfur Fires and Explosions," NFPA 655, 1988 Edition. xx
27. U.S. Department of Health and Human Services, Public Health Service Centers of Disease Control, National Institute for Occupational Safety and Health, "NIOSH, Health Hazard Evaluation Report," HETA 82-292-1358

28. Manufacturing Chemists' Association, Inc., "Properties and Essential Information for Safe Handling and Use of Sulfur," Chemical Safety Data Sheet SD-74.

29 McBee, W.C., personal communication to G.R. Darnell, EG&G Idaho, Inc., May 31, 1991.

30. Schmidt, W.B., U.S. Department of the Interior, Bureau of Mines, Washington, D.C., personal communication to G.R. Darnell, EG&G Idaho, Inc., April 5, 1991.

31. Darnell, G.R., EG&G Idaho, Inc., personal communication to Mr T. L. Clements, Mr. J. A. Logan, and Mr. J. D. McKinney, "Trip Report, Presentations at First International Mixed Waste Symposium," GRD-28-91, September 23, 1991.

32. Darnell, G.R., EG&G Idaho, Inc., Personal communication to Distribution, Trip Report, U.S. Bureau of Mines Testing of Sulfur Polymer Cement Towards Environmental Improvement, November 20, 1991.

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