

SULFUR POLYMER CEMENT,  
A SOLIDIFICATION AND STABILIZATION AGENT FOR  
RADIOACTIVE AND HAZARDOUS WASTES<sup>a</sup>

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SUMMARY

There are no known perfect solidification and stabilization agents for radioactive or hazardous wastes, so the search continues for individual agents for specific wastes. The U.S. Department of Energy began testing sulfur polymer cement (SPC) as a radioactive and hazardous waste solidification and stabilization agent because of its unusual properties. SPC is a sulfur polymer composite material that begins melting between 110 and 120°C (230 and 248°F), with an optimum pour temperature between 130 and 140°C (266 and 284°F). The compressive strength of SPC upon cooling averages 27.6 MPa (4,000 psi). Its mechanical strengths continue to increase for at least two years to approximately triple the original strength. As a proven construction concrete, SPC has demonstrated the ability to survive for years in acids and salts that destroy or severely damage hydraulic concretes in months or even weeks.

Perhaps SPC's strongest selling point is that it will always melt and pour at approximately 135°C. This feature will allow hazardous or radioactive waste specimens that do not pass the required tests to be remelted and reformulated until they do pass.

Heavy loadings (5 wt%) of the eight toxic metals have been combined individually with SPC and 7 wt% sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ). The leach rates for mercury, lead, chromium, and silver oxides were reduced by six orders of magnitude, while arsenic and barium were reduced by four. With ever increasing emphasis on high-temperature treatment of radioactive and hazardous wastes, the ability of SPC to stabilize incinerator ash and its volatilized toxic metal contents is encouraging.

All SPC used in tests to date was formulated for the construction industry. The preceding tests and many others conducted in other countries like Denmark, Japan, France, Germany, and the Netherlands strongly suggest that SPC shows great promise for further development. Ion-exchange resins that failed miserably in routine SPC testing passed in excellent fashion when the temperature and duration of heating was increased. An additive dramatically improved the leach resistance for toxic metals. The search is just beginning for different configurations of SPC that can accommodate higher loadings of various difficult-to-stabilize wastes.

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## ACRONYMS AND TERMS

The correct terms for the substances addressed in this paper are "modified sulfur cement" and "sulfur polymer cement." These two terms are synonymous, and for clarity are given the single acronym "SPC." The acronym for sulfur polymer cement concrete is "SPCC." The words "cement" and "concrete" refer to the generic family of hydraulic cements and concretes, while "PCC" refers to the specific concrete known as Portland cement concrete. Hazardous waste that is also radioactively contaminated is called mixed waste.

## INTRODUCTION

Within the U.S. Department of Energy (DOE), solidification and stabilization agents for low-level radioactive waste (LLW) and mixed waste were failing to pass governmental tests at unacceptable rates, or were passing the tests with low waste-to-agent ratios. Recognizing that problem in the early 1980s, DOE's Defense Low-Level Waste Management Program sought other potential waste solidification and stabilization agents that might supplement or replace concrete. SPC was selected for testing. The ability of SPCC to withstand attack by most acids and salts that destroy concrete offered strong evidence that SPCC might perform better in stabilizing waste for long periods of time than concrete.

NOTE: Portland cement has been used for five decades as the principal radioactive waste solidification agent and thus, is accepted as the standard of comparison for other waste solidification and stabilization agents.

With waste stabilization and minimization as the primary goals in waste disposal, DOE's Defense Low-Level Waste Management Program funded research and testing of SPC laden with LLW at Brookhaven National Laboratory (BNL). DOE's Hazardous Waste Remedial Action Program (HAZWRAP) added funding later. This paper summarizes these and other tests.

## DEVELOPING AND TESTING COMMERCIAL SPC AND SPCC FOR HARSH CHEMICAL ENVIRONS

Pertinent data provided by commercial tests of SPC and SPCC are vital to understanding SPC's potential for stabilizing LLW, mixed waste, and hazardous wastes.

### Developmental Background

In 1972, the Bureau of Mines discovered that the addition of dicyclopentadiene and oligomers of cyclopentadiene in equal quantities totaling 5 wt% of the sulfur phase resulted in a construction concrete having advantageous properties not found in other concretes.<sup>1,2,3</sup> The Bureau of Mines and the Sulphur Institute joined forces. In 1973, the Sulphur Development Institute of Canada joined the effort.<sup>4</sup>

### Properties of SPC and SPCC

SPC and SPCC will melt every time their temperatures are elevated to approximately 115°C (235°F). When heat is removed, they will regain their original strength very rapidly (upon cooling). The various mechanical strengths of SPCC are approximately double those of routine 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 27.6 MPa (4,000 psi), SPCC reaches that approximate strength upon cooling. In two years, its strength can increase by a factor of three.<sup>6</sup>

SPC was found to be impermeable to water in laboratory tests.<sup>4</sup> While both SPC and concrete have approximately the same volume of pores (void space), the pores in SPCC are not connected, whereas the pores in concrete are. The U.S. 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 an approximately 7.5-mm (1/4-in.)-thick lining of SPC on mine walls. The SPC lining proved impermeable to radon gas.<sup>7</sup>

However, any of the following events will allow both water and gas to penetrate solidified SPCC to varying degrees: (a) if the SPCC is cooled too quickly, it will contain an excess of voids that will connect with each other, (b) if the aggregate in the SPCC contains water, tiny steam vents will develop, or (c) if the wrong aggregate or waste is used, SPCC will become more porous. Fortunately, cooling of the SPCC mass can be controlled with precision,<sup>8</sup> water can be routinely eliminated prior to the pour, and the additions of SPCC  $Al_2O_3$  or  $Fe_2O_3$  will improve the impermeability of SPCC while reducing the emissions of  $SO_2$ .<sup>6</sup> With a given aggregate, SPCC will be less permeable than concrete.

Sulfates attack PCC, but have little or no effect on the integrity of SPCC.<sup>1,2</sup> SPCC 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</sup> Shrinkage, on the average, is 0.1%, slightly greater than PCC. SPCC 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 in SPC is roughly half that in PCC. Where SPCC and PCC are made with the same aggregate, their densities are nearly identical. Viscosity of SPC is between 25 and 50 cp at 135°C (275°F).

SPCC is best used where exposed to high concentrations of mineral acids, corrosive electrolytes, salt solutions, or corrosive atmospheres in general.<sup>6,5,9</sup> After being exposed to sulfuric acid solutions and copper electrolytic solutions for nine years, SPCC showed no evidence of corrosion or deterioration. In a six-year test in a chemical processing plant, PCC was attacked and completely destroyed in some cases, while SPCC showed practically no evidence of strength loss or material degradation. After seven years of exposure to a salt environment in a test at a potash chemical storage building, two SPCC structural support piers were undamaged, while the PCC pier in the same location was heavily damaged after only two and a half years.

SPCC has its faults. In construction applications, SPCC 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%). SPCC is not recommended for placement in areas handling strong bases, strong oxidizing agents, or aromatic or chlorinated solvents.<sup>2</sup>

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

In the 1980s, DOE funded BNL to research, test, and develop SPC to EPA and U.S. Nuclear Regulatory Commission (NRC) requirements. This section discusses those and other efforts.

## Tests Completed to EPA Standards

SPC requires no chemical reaction for solidification; it will always solidify when it cools below the melt point and will accept a wide range of waste (aggregate) with divergent chemical and physical compositions. SPC is easier to use than thermoplastics, like polyethylene, because of SPC's low viscosity and low-melt temperature.<sup>1</sup>

Mixed waste fly ash with a pH of 3.8 contained the following, which are 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>10,11</sup> 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 submitted to the EPA's extraction procedure toxicity (EP Tox) test, and to the toxicity characteristic leaching procedure (TCLP). With a loading of 40 wt% flyash, both cadmium and lead were still above the concentration limits allowed under the Resource Conservation and Recovery Act (RCRA), so additives were sought that would further reduce the mobility of the toxic metals. Sodium sulfide ( $\text{Na}_2\text{S}$ ) was selected because it reacts preferentially with cadmium and lead (toxic metals) to form highly insoluble metal sulfides. The resultant monolith passed the EPA's EP Tox test and the TCLP, thus meeting the criteria for a delisting petition as hazardous waste.

The need for incineration/vitrification of troublesome wastes before introduction to any solidification agent has long been recognized by the EPA<sup>12</sup> and DOE. Based on the preceding successes and the need for high-temperature waste, tests were set up by the author. Mercury and its compounds are the most troublesome, and volatilization rates can approach 100%. Toxic metal oxides become secondary waste streams that must be captured and stabilized in a separate medium. SPC not only serves as an encapsulation material suitable for toxic metal oxides, but also causes chemical conversions from the highly leachable metal oxide form to the unleachable or leach-resistant forms of metal sulfides and sulfates. The addition of 7 wt% sodium sulfide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) to the SPC mixture further enhanced the conversion factor. The potential for leaching mercury, lead, silver, and chromium was reduced by six orders of magnitude. Arsenic and barium were next with four orders of magnitude. Cadmium and selenium were less responsive.<sup>13</sup>

## Tests Completed to NRC Standards

The NRC has established a qualifier list of tests under the title "Waste Form Qualification Testing." After the immersion test was completed, compressive strengths of waste-impregnated SPCC ranged from a low of 13.8 MPa (1,998 psi) for 40 wt% boric acid, to a high of 44.4 MPa (6,435 psi) for 40 wt% incinerator ash, with sodium sulfate falling in between. Compressive strength tests after freeze-thaw cycling were well above the NRC limit, and there were some insignificant increases and decreases in strength with different wastes.

The waste contained Co-60 and Cs-137 and was leached for 90 days in compliance with American Nuclear Society (ANS) 16.1. The leach rate was found to be lower for incinerator hearth ash (14.6) than for highly soluble sulfate salts (9.7). The leach rates were some four to eight orders of magnitude lower than the minimum leach index (6) established by the NRC. The conclusion was that radionuclides in SPC leach very slowly.<sup>11</sup>

The NRC tests for biodegradation of SPCC were completed successfully with "no growth" being the result of both the American Society for Testing and Materials (ASTM) G-21 and ASTM G-22 tests. The NRC irradiation test to  $10^8$  rad was completed successfully. Initially, some deterioration was detected in the SPCC and mixed waste fly ash combination when subjected to the immersion test, but that problem was corrected by the addition of 0.5 wt% glass fibers.<sup>10</sup>

SPCC specimens containing 80 wt% loadings of lead oxide were successfully subjected to  $10^8$  rad at Oregon State University as prescribed in the NRC irradiation test. The specimens actually gained 1,000 psi during the irradiation test, and were an order of magnitude better than NRC requirements.<sup>b</sup> No gas generation was noted. The original intent was to test lead-laden SPCC as a possible shielding for personnel in high-radiation areas.

In the Netherlands, scientists subjected SPC final waste forms to  $10^8$  rad and also found that the specimens gained strength. During the irradiation tests, no gaseous radiolysis products were detected.<sup>6</sup> Inorganic waste and SPC are essentially insensitive to radiation. The constituents that cause radiation effects in the hydraulic or bitumen waste forms are not present in SPC.

The Netherlands Energy Research Foundation ECN, and BNL, dried ion-exchange resins and combined them with SPC. In the worst case, the test specimen crumbled in three days by absorbing moisture from the air (60 to 80% humidity). The Netherlands tried another technique. They combined the resins with SPC and raised the temperature  $100^\circ\text{C}$  to  $220^\circ\text{C}$ - $250^\circ\text{C}$  in the presence of asbestos or diatomite for three hours. The resultant test specimen was immersed in water for one year and showed no signs of deterioration.<sup>6</sup>

The author has completed a series of full-scale nonradioactive tests with different mixers in an effort to select one that can be used for the NRC's full-scale tests with mixed waste, and afterwards as an operational SPC mixer.<sup>8</sup>

Research and development has resulted in a modified SPC that can stabilize waste types like dehydrated boric acid salts, incinerator hearth ash, mixed waste fly ash, and dehydrated sodium sulfate salts that have previously defied solidification and stabilization in concrete in any significant quantity. The modified SPC offers a monolithic waste form that is durable in harsh environments.<sup>11</sup>

Comparative test results show that a given volume of waste requires less SPC than cement to achieve a stabilized final waste form that will satisfy EPA and NRC requirements. The following numerical advantages of SPC over cement were calculated: 6.7 times less SPC with sodium sulfate, 3.6 times less SPC with boric acid, 1.4 times less SPC with incinerator bottom ash, and 2.7 times less SPC with incinerator fly ash.<sup>11</sup> The average was 3.3 times less SPC than cement.

Since the NRC requires only 500 psi compressive strength, and since the SPCC, which contained various waste, averaged approximately 4,000 psi,<sup>1</sup> there is a large "window of opportunity" for experimentation to develop the optimum SPC mixture for given waste forms.

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b. Test results confirmed in a telecommunication with Mr. William C. McBee, irradiation test manager, June 4, 1991.

## Waste Streams That Cannot be Combined with SPC for Stabilization

Combining sodium nitrate salts with SPC is not recommended because when the two compounds are combined, they could cause a "potentially reactive mixture."<sup>11</sup> SPC is not compatible with highly soluble compounds or organic materials. Expanding clays cannot be used in SPCC for the same reason.<sup>2</sup> Chemical corrosion of the final waste form occurs when placed in strong alkaline solutions (above 10%), strong oxidizing solutions like chromic acid and hypochlorite solutions, and some metal slimes like copper.

### SAFETY AND ALARA CONSIDERATIONS

Sulfur is the chemical industry's most widely used raw material<sup>14</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>15</sup> National Fire Protection Association,<sup>16</sup> U.S. Department of Health and Human Services,<sup>17</sup> National Institute for Occupational Safety and Health, and Manufacturing Chemists' Association, Inc.<sup>18</sup>

Airborne SPC dust can be mildly explosive if all conditions are optimal (normal safety precautions are not exercised); therefore, SPC is procured in pellet or wafer form, which provides handling capabilities with minimal creation of dust. SPC and SPCC will emit hydrogen sulfide gas ( $H_2S$ ) and sulfur vapor to the off-gas system if excessive temperatures are created. Normal heat control systems with backup gas detectors will prevent a safety hazard.<sup>15,16,17,18</sup> The recommended mixing temperature for SPCC is 127–138°C (260–280°F), which will minimize gaseous emissions to the off-gas system and provide optimum viscosity.

SPC and SPCC are nontoxic<sup>19</sup> and do not meet any of the criteria for flammability as established by the United Nations or the U.S. Department of Transportation. SPC's flash point, as determined by the Cleveland open cup method, is 177°C (350°F), and the autoignition is 232–254°C (450–490°F). SPC and SPCC will burn if held in a flame, but will self-extinguish when the heat is withdrawn.<sup>2,5</sup> Their poor thermal conductivity (0.2 to 0.5 BTU/h ft °F) is a strong deterrent to melting.

SPCC offers self-shielding that reduces the radiation exposure of operators over that experienced in handling the same waste before it is microencapsulated in SPCC. Since SPCC will accommodate three to four times more waste than PCC, handling by operators and radiation exposure is reduced accordingly because of fewer handlings of containers.

### CONCLUSIONS

From the beginning, we sought the problems associated with SPC, and have been pleasantly surprised at each new promising finding. SPC is a new solidification and stabilization agent; the oldest documented specimens are 15 years old. In order to establish acceptable longevity, SPC is being tested and evaluated in the laboratory for phase changes, etc. Those unreleased tests are encouraging at this time. The principal value of SPC is in these areas: greater waste-to-agent ratio than concrete, no need to empty mixer after the pour, can remelt and reformulate SPC to pass required tests, less permeable than concrete, no water in the final waste form, low temperature process, and less radiation exposure to workers.

What remains is SPC formulation development for different troublesome wastes, and determination of which wastes are best placed in SPC. With high-temperature processes being

the favored treatment, SPC should be the "clean up" agent that will readily accommodate the high concentrations of toxic metals, most notably lead and mercury, in the resultant ash and off-gas system residue.

In determining cost and environmental advantages, the volume-reduction factor offered by SPC will be abundantly clear in the ever increasing high cost of mixed waste disposal. Additionally, the lack of water in the SPCC final waste form offers less chemical breakdown, less biodegradation, less leaching, and less gas generation after disposal. In general, the public should benefit environmentally and economically from the use of SPC.

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