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STABILIZATION OF LIQUID LOW-LEVEL AND MIXED WASTES: A TREATABILITY STUDY

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ABSTRACT

A treatability study has been conducted on liquid low-level and mixed wastes using the stabilization agents Aquaset, Aquaset II, Aquaset II-H, Petroset, Petroset-H, and Petroset II. A total of 40 different waste types with activities ranging from 10^{-14} to 10^{-4} curies/ml have been stabilized. Reported data for each waste include its chemical and radiological composition and the optimum composition or range of compositions (weight of agent/ volume of waste) for each stabilization agent used. All wastes were successfully stabilized with one or more of the stabilization agents and all final waste forms passed the Paint Filter Liquids Test (EPA Method 9095).

INTRODUCTION

Over the years, Sandia National Laboratories/New Mexico (SNL/NM) experimental research has generated a collection of small-volume liquid low-level and mixed wastes that include acids, bases, solvent mixtures, expired radiological standards, lubricants, pump oils, and liquids that have acquired radioactive and/or Resource Conservation and Recovery Act (RCRA) listed contaminants as a result of being exposed to a particular environment (e.g., liquids used in radiation decontamination).

The Liquid Waste Stabilization Treatability Study was designed to utilize the existing SNL/NM liquid low-level and mixed low-level waste inventory to develop standardized liquid waste stabilization procedures that would then be available for use by generators to stabilize liquid low-level and mixed low-level wastes. Stabilized wastes could then be picked up by the SNL/NM waste management group and would ultimately be disposed of at either the Nevada Test Site low-level waste disposal facility or a mixed waste disposal facility, as appropriate.

Stabilization immobilizes heavy metals by chemically binding them in a solid matrix. This decreases the potential for metals to leach out after disposal if the waste were to be exposed to moisture or weak acids. The two most common stabilization agents used to immobilize inorganic solids and aqueous liquids are Portland cement and lime/pozzolan. However, for this study, a series of compounds consisting primarily of either Montmorillonite clays or a mixture of Montmorillonite and cement that are sold under the trade names Aquaset and Petroset by Fluid Tech, Inc. of Las Vegas, Nevada were used. The stabilization agents Aquaset, Aquaset II, Aquaset II-H, Petroset, Petroset-H, and Petroset II, were chosen for several reasons:

- Reagents are particularly suitable for wastes that contain both organic and inorganic components in aqueous solution (Aquaset II, Aquaset II-H, Petroset, Petroset-H).
- Reagents can be combined to stabilize immiscible organic and aqueous layers (Aquaset II or Petroset with Petroset II).

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DISCLAIMER

- Petroset II is specifically designed to stabilize waste oils, solvents and other nonaqueous liquids.

- Unlike Portland cement, all reagents except Aquaset II-H and Petroset-H set up to final waste form and consistency in less than 24 hours. The "H" reagents, which contain cement, set up to the hardness of concrete in less than a week, usually 2-4 days.

- Wastes stabilized with Petroset have met the Waste Acceptance Criteria for disposal at the Nevada Test Site. Sandia's Waste Treatment Plan specifies that its low-level waste will ultimately be disposed of at the Nevada site.

WASTE IDENTIFICATION AND CHARACTERIZATION

Generators or current owners of liquid low-level and mixed wastes were interviewed and asked to complete a Process Knowledge Evaluation (PKE) form in order to determine how much characterization data was already available for each waste. Data necessary for stabilization include waste surface radiation dose rate, total activity of radionuclide(s) present, chemical constituents, and pH, if an aqueous phase is present. When the required information was unknown, or data were of questionable quality and could not be verified through the PKE process or written analytical records, waste samples were sent for the necessary analyses. Unless the information was obtained from the PKE, prior to acceptance for stabilization, a gamma spectrum was obtained for each waste to determine the type and activity level of radionuclides present. If tritium was known or suspected to be present, and the waste was not a dated and sealed radiological standard for which the level of radioactivity could be calculated, a tritium analysis was also performed. Samples of wastes that were suspected to be mixed due to the presence of organic or toxic metal contaminants as well as radioactive constituents were sent to Mountain States Analytical in Salt Lake City, UT for analysis of toxic metal constituents, volatile organic, and semi-volatile organic constituents. If concentrations of hazardous constituents were such that stabilization was no longer the most appropriate treatment (e.g., high concentrations of organics would dictate incineration), these wastes were removed from the study.

Only wastes whose radiation dose rates were less than 100 mrem/hr at the surface of an unshielded container and less than 10 mrem/hr one foot from the surface of the container were accepted for this study. While wastes with higher radiation levels could be stabilized using the procedures developed during this program, they would have to be neutralized and stabilized in a shielded environment such as a glove box, rather than in a hood or open laboratory. Such a shielded environment was not available in the area where this study was conducted.

Almost all of the mixed low-level liquid waste at SNL/NM consisted of radiological standard solutions that were hazardous only because they were either strongly acidic or basic. Once neutralized, these wastes became low-level radioactive wastes that were stabilized for disposal at a low-level waste disposal facility. A brief description of the wastes stabilized during this study is provided in Table I.

STABILIZATION AGENTS

The physical and performance characteristics of each stabilization agent are summarized in the following discussion. A more detailed description of the uses of each may be found in Reference (1).

Table I. Liquid Waste Stabilized with Fluid Tech Reagents

Waste Description	Volume, ml	Radionuclide(s) Present *
100 µg/ml uranium in 10% nitric acid	500	U-238, Th-234, Ra-226
1000 µg/ml uranyl nitrate in 2% nitric acid	1000	U-238, Th-234, U-234
100 ppm uranyl oxide, <0.5 wt % titanium dioxide, <30 ppm salicylic acid in water	7600	U-238, Th-234, Bi-214, U-235, Th-231
Tritiated water	587	H-3
Thorium nitrate in acid	400	Th-232, Ra-228, Ac-228, Th-228, Ra-224, Pb-212, Bi-212, Tl-208
35%, 10% and 3% nitric acid solutions	2090	Zn-65
999 µg/ml uranyl nitrate in water	500	U-238, Th-234, U-234, U-235
Ra-226 standard in acid	5	Ra-226
0.05 N sodium hydroxide	7600	U-234, Am-243, Co-60, Cs-137, K-40
Glycerin in water	7600	H-3
Sodium chloride in water	9000	Na-22, Am-241
Co-60 in 0.1 N hydrochloric acid	110	Co-60, K-40
Cs-134 in 0.1 N hydrochloric acid	30	Cs-134
Cs-137 in 0.1 N hydrochloric acid	492	Cs-137
10 ppm uranium in 4 N nitric acid	500	U-234, Th-228, Bi-212, U-235, Th-231
1000 ppm uranium in 2% nitric acid	500	U-238, Th-234, U-234, U-235, H-3
Mixture of: 200 ppm uranium in 5% nitric acid, 100 ml 2 ppm uranium in 5% nitric acid, 100 ml 1000 ppm uranium in 2% nitric acid, 100 ml 5 mg/g U-238 in water, 5 ml Uranium mixed isotopes in water, 2 ml	307	U-238, Th-234, Ra-226, Sr-85, U-235, K-40, Th-231
Sr-90 in 1% nitric acid	100	Sr-90, H-3
Ru-106 in 1 N hydrochloric acid	100	Ru-106, H-3
Ra-226 in 2% hydrochloric acid	820	Ra-226, Pb-214, Bi-214
Mixture of Ra-226 solutions: Ra-226 in 2% hydrochloric acid, 180 ml Four 20-ml ampules 5.072 µg/ml Ra-226 , 100 ml 5 µg/ml Ra-226, 50 ml	410	Ra-226, Pb-214, Bi-214, Pb-210, H-3
Pu mixed isotopes in acid	23	Calculated Pu activity: 3.67 nCi/ml, Pb-214, Am-241
Am-241 in 3 N nitric acid	31	Am-241, H-3
Pb-210 in acid	2	Pb-210, Cs-137
Np-237 in acid	1	Np-237, Pa-233, Cs-137, Sr-85
Pm-147 in acid	3	Pm-147
Tl-204 in acid	2	Tl-204

Table I, Continued

Waste Description	Volume, ml	Radionuclide(s) Present *
995 µg/ml uranium in 2% hydrochloric acid	500	U-238, Th-234, U-234, U-235
1000 µg/ml thorium in 10% hydrochloric acid	500	Th-232, Ra-228, Ac-228, Th-228, Ra-224, Pb-212, Bi-212, Tl-208
Mixture of: 1000 ppm uranyl nitrate in water, 100 ml 995 µg/ml uranium in 2% hydrochloric acid, 500 ml	600	U-238, Th-234, U-234, U-235
100 µg/ml lanthanum, dysprosium, yttrium and uranium	500	La-138, Dy-154, U-238, Th-234, U-235
1 ppm uranium in acid	750	U-238, Th-234
Uranyl nitrate in acid	100	U-238, Th-234, U-234, U-235, Th-231
Mixture of 0.025 M hydrochloric acid and 0.002 - 0.005 diamino propionic acid	12,100	Cs-137
Uranyl nitrate in water	250	U-238, Th-234, U-234, Ra-226, U-235
Supersaturated (~ 20 N) sodium hydroxide	130	Cs-134, Cs-137, K-40
Potassium chloride in water	20	Cs-134, Cs-137, Eu-154, Be-7
Silver chloride in water	50	Cs-134, Cs-137, K-40
Deionized water	5700	Ce-144, Cs-134, Cs-137, Eu-154, Tl-132
Lubricating oil	20	Cs-134, Cs-137, K-40
Simple Green in water	28,500	K-40, Mn-54, Na-22, Zn-65
0.1 M hydrochloric acid	20,000	Co-57, Co-60, Y-88, Ba-133, Cs-137
1.0 M hydrochloric acid	1800	Co-60, Cs-134, Cs-137, Mn-54, Ce-144
0.5 M hydrochloric acid	3150	Ba-133, Co-60, Cs-134, Cs-137, Ru-106, Zn-65
Sr-90 in water	50	Sr-90
Dilute ammonium hydroxide (pH ~8)	280	Ra-226, K-40
Concentrated ammonium hydroxide	5000	K-40
Glacial acetic acid	1750	K-40
Concentrated sulfuric acid	1200	K-40
Concentrated hydrochloric acid	2000	K-40
Concentrated nitric acid	2375	K-40
10% oxalic acid	350	H-3

* Waste radioactivity ranged from 10^{-14} to 10^{-4} Ci/ml. Most liquids had total specific activities in the nCi/ml range.

Aquaset is a granular stabilization agent that falls within a -4 to +10 US MESH size and is used to stabilize aqueous solutions containing up to 5% (by volume) oils or organic compounds. Aquaset is not normally mixed with other stabilization agents.

Aquaset II is a powdered stabilization agent of which 80-85% can pass through a 200 US MESH screen. It is best suited for stabilizing aqueous solutions with high dissolved solids, such as neutralized acids and bases, and/or other liquids (such as alcohols, benzenes, glycols and low molecular weight ketones) that are water-soluble or miscible. Aquaset II is particularly useful in treating mixed wastes that contain both heavy metals and water-miscible organic compounds. It can be used in conjunction with Petroset or Petroset II. Final waste form is a stiff but flexible clay, whose stiffness is directly proportional to the amount of Aquaset II used.

Aquaset II-H is used for the same wastes as Aquaset II; however, it sets up more slowly (several days), and sets up to a hard, concrete-like matrix. Both Aquaset II-H and Petroset-H (see below) may provide more effective protection against leaching of toxic metals than their "non-H" counterparts.

Petroset is a powdered stabilization agent of which 80-85% can pass through a 200 US MESH screen. It is best suited for stabilizing wastewater that is mixed with organics, oils, or solvents. It is commonly used in conjunction with Aquaset II (when both organics and salts are present) or Petroset II, and can be used for the same aqueous solutions that would be suitable for stabilization with Aquaset. Petroset can also be used to treat aqueous sludges and particle suspensions. With the addition of small amounts of water, it can stabilize dry solids such as powders. Final waste form is the same as Aquaset II.

Petroset-H is used for the same waste types as Petroset, and, like Aquaset II-H, it sets up to a hard, concrete-like matrix in less than a week.

Petroset II is a powdered stabilization agent that can pass through a 200 US MESH screen and will stabilize most hydrocarbon waste fluids. Petroset II will not stabilize aqueous fluids. It can be used with Aquaset II and Petroset when the waste is an immiscible mixture of oils and aqueous liquids. The final waste form has a consistency analogous to that of putty or plastic wood.

STABILIZATION PROCEDURES

Aqueous liquids must have a pH between 5.0 and 11.0 prior to stabilization with Aquaset and Petroset agents. The manufacturer recommends sodium hydroxide (Na OH) for acid neutralization and phosphoric acid (H_3PO_4) for bases. In this study, 5N NaOH was used to bring dilute acidic solutions into the required pH range. Concentrated acids were neutralized using a combination of solid and 5N NaOH to minimize the increase in waste volume. All bases were neutralized with concentrated H_3PO_4.

Since one of the goals of this study was to gain as much information as possible on the variety of agents and the amounts of each required to stabilize a waste type, whenever there was sufficient volume of a particular waste, multiple agents and concentrations (g agent/100 ml waste) were used. For "large-volume" ($\geq$ 1 liter) wastes, for each stabilization agent tested, three 200-ml samples were prepared: one containing the manufacturer's recommended concentration of stabilization agent, one with 75% of the recommended concentration and one with 133% of the recommended concentration. These concentration range endpoints are also recommended by the manufacturer.

Based on visual inspection of final waste forms, an "optimum" concentration was selected for the agent(s) felt to be most suitable for each waste; these concentration(s) and agent(s) were then used to stabilize any remaining waste. For "H" reagents, the optimum concentration was the amount sufficient to produce a cement-like final form in 2-4 days. For the remaining reagents, it was the concentration that produced a final clay-like form within 24 hours of mixing that was still somewhat flexible, but stiff enough that it would not readily extrude under normal pressures that might be experienced in a disposal facility (approximately 12 psi for 15 ft of overburden). Some final waste forms passed the Paint Filter Liquids Test, but were sufficiently plastic that extrusion under pressure was deemed a possibility. "Small-volume" (<1 liter) wastes were initially stabilized with the manufacturer's recommended agent concentration. If, after standing covered, but not sealed, for 24 hours, it was obvious that the waste form would not pass the Paint Filter Liquids Test, up to 33% more (by weight) stabilization agent was added.

With the exception of Aquaset, which is not mixed but merely added to the liquid in roughly one-third increments at ten-minute intervals, the stabilization agent was added to the waste liquid with stirring. Small volumes were manually mixed to a homogeneous consistency using a metal spatula. Volumes greater than 1 liter were mixed using a mixer attachment on a hand-held half-inch electric drill. Since the latter procedure was effective for volumes up to about 2.5 liters, unless they were stabilized with Aquaset, larger volume wastes were split into smaller batches prior to stabilization. The mixing procedure is illustrated in Figure 1, and representative final waste forms for each stabilization agent are shown in Figure 2.

Fig. 1. Stabilization of Liquid Waste

After stabilization agent addition and mixing, (all agents except Aquaset), wastes were covered, but not sealed, and allowed to stand for 24 hours before being tested for free liquid using the Paint Filter Liquids Test, EPA Method 9095 (2). In most cases, wastes stabilized with Aquaset II-H and Petroset-H were sufficiently "set" to be tested after 24 hours; however, they did not usually achieve a cement-like consistency until 1-3 days later.

RESULTS

The stabilization agents used to immobilize each waste type listed in Table I are summarized in Table II. The choice of an "optimum" concentration was based on the minimum concentration of agent that either resulted in a cement-like final form for "H" agents, or, as previously discussed, a stiff clay for the "non-H" agents. When there was no obvious difference in final waste form consistency, a range of concentrations was considered to be "optimum". If significantly less of a particular agent was required to produce a suitable final form, this was deemed the "optimum" agent.

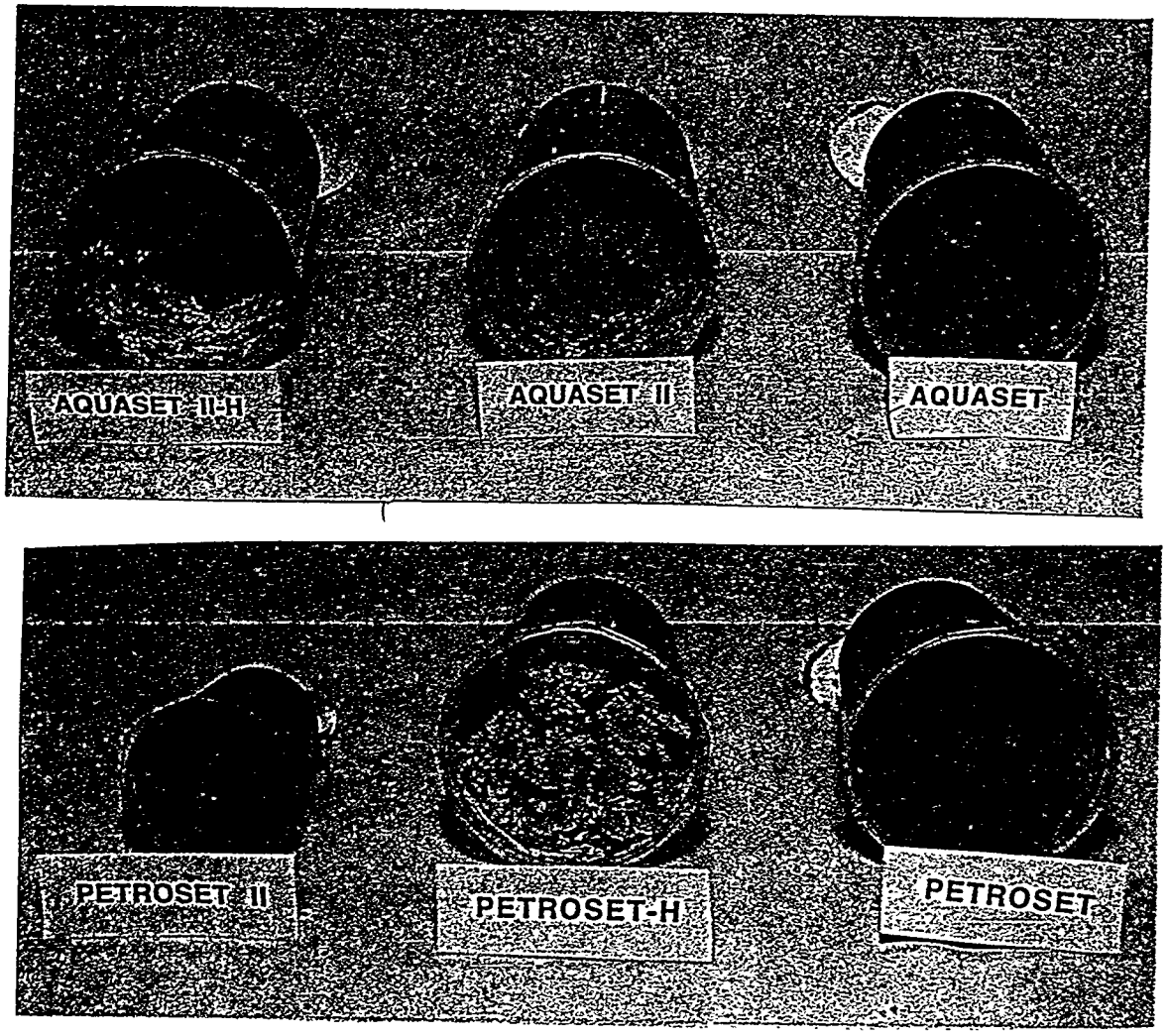

Fig 2. Final Waste Forms

In general, the agents Aquaset II, Aquaset II-H, Petroset and Petroset-H were all equally suitable for dilute (low ionic strength) solutions, such as the 0.1 M hydrochloric acid, 0.1 M sodium hydroxide, and dilute ammonium hydroxide solutions. As the ionic strength of the neutralized solution increased (concentrated acids and bases), Petroset and Petroset-H did not perform as well as Aquaset II and Aquaset II-H. As noted in Table II, using the recommended amount of Petroset did not always produce a final waste form that passed the Paint Filter Liquids Test, and Petroset-H often took as long as a week to set up.

Table II. Waste Stabilization Data Summary

Waste	Agent(s) Used	Concentration, g/100 ml	Optimum Agent(s)	Optimum Concentration, g/100 ml
Std U, Th solutions in acid (nitric, hydrochloric) or water	Aquaset II Aquaset II-H Petroset Petroset-H	67, 72 78, 96 60, 68*, 92 84,100	Aquaset II Aquaset II-H Petroset-H	67 - 72 78 - 96 84
Uranium oxide, titanium dioxide, and salicylic acid in water	Aquaset II Aquaset II-H Petroset Petroset-H	45, 60, 72, 80 60, 72, 84, 112 45, 60, 80 60, 84, 112	All acceptable	60 84 80 84
Tritiated water, deionized water	Aquaset Petroset Petroset-H	45, 60, 80 60 84	All acceptable; Aquaset preferred; no mixing req'd	60
Concentrated sulfuric acid	Aquaset II Aquaset II-H Petroset-H	45, 60, 80 63, 84, 112 63, 84, 112	Petroset-H	All acceptable
Ra-226 in acid	Aquaset II Aquaset II-H Petroset-H	68 92 76*, 103	Aquaset II Aquaset II-H	N/A; only one concentration used
0.1 M sodium hydroxide, dilute ammonium hydroxide	Aquaset II Aquaset II-H Petroset Petroset-H	54, 72, 96 72, 96, 128 45, 60, 90 62, 84, 112	All acceptable	72 72 - 96 90 84
Glycerin in water	Aquaset II Aquaset II-H Petroset II	45, 60, 80 63, 84, 112 60**	Aquaset II Aquaset II-H	80 84
Sodium chloride in water	Aquaset II Aquaset II-H Petroset Petroset-H	45, 60, 80 63, 84, 112 45*, 60, 80 63, 84, 112	Aquaset II Aquaset II-H Petroset-H	60 84 84
Small-volume rad stds (Co-60, Cs-134, Cs-137, Sr-90, Ru-106, Pu, Am-241, Pb-210, Np-237, Pm-147, Tl-204, La-138, Dy-154) in acid	Aquaset II Aquaset II-H Petroset-H	41, 72, 94 91, 96 84	All acceptable	72 91 - 96 N/A; only one concentration used
Mixture of 0.025 M hydrochloric acid and 0.002 - 0.005 M diamino propionic acid	Aquaset II Aquaset II-H Petroset Petroset-H	54, 72, 96 72, 96, 128 45, 60, 90 63, 84, 112	All acceptable	72 72 60 63
Supersaturated (~20 N) sodium hydroxide	Aquaset II-H	90	N/A; only one used	N/A; only one used

Table II, Continued

Waste	Agent(s) Used	Concentration, g/100 ml	Optimum Agent(s)	Optimum Concentration, g/100 ml
Mixture of silver chloride, potassium chloride in water and Ultima Gold *** (immiscible layers)	Aquaset II and Petroset II	72 36	N/A; only one combination used	N/A; only one combination used
Sodium hydroxide in Ultima Gold ***	Petroset II	36	N/A; only Petroset II can be used for organics	N/A; only one used
Simple Green in water	Aquaset	45, 60, 80	N/A; only one used	60
Rad stds in 0.1 M hydrochloric acid	Aquaset II Aquaset II-H Petroset Petroset-H	60 72 60 84	All acceptable	Concentrations used considered optimum based on earlier testing
Sr-90 in water	Petroset	60	N/A; only one used	N/A; only one used
Concentrated hydrochloric acid	Aquaset II Aquaset II-H Petroset Petroset-H	54, 72, 96 64, 72, 96 45*, 60*, 80 63*, 84*, 112	Aquaset II Aquaset II-H	72 96
Glacial acetic acid	Aquaset II Aquaset II-H Petroset Petroset-H	54, 72, 96 64, 72, 96 45, 60, 80 63, 84, 112	Aquaset II Petroset Petroset-H	72 80 112
Concentrated nitric acid	Aquaset II Aquaset II-H Petroset Petroset-H	54, 72, 96 72, 96, 128 96, 109, 127 63, 84, 112	Aquaset II Aquaset II-H Petroset-H	72 96 84
10% oxalic acid	Aquaset II Aquaset II-H	72 96	Both acceptable	Concentrations used considered optimum based on earlier testing
Concentrated ammonium hydroxide	Aquaset II Aquaset II-H Petroset Petroset-H	65, 72, 96 72, 96, 128 45*, 60*, 80* 63*, 84, 112	Aquaset II Aquaset II-H	72 96

* Too runny; did not pass Paint Filter Liquids Test.
** Mixture did not set up. 36 g/100 ml Aquaset II was added; final form passed the Paint Filter Liquids Test.
*** Ultima Gold is a nonhazardous organic reagent for scintillation counting.

Although concentrated acids and bases were diluted with 2 parts water/1 part waste prior to neutralization, the corresponding sodium salts still precipitated out of solution with neutralization. The salts were filtered off, leaving essentially saturated sodium salt solutions to be stabilized. The type of anion present (sulfate, chloride, nitrate, etc.) had a

significant effect on agent performance. (See data, Table II.) Most notable was the behavior of the saturated sodium sulfate solution from the neutralization of concentrated sulfuric acid. The high sulfate concentration did not affect the final waste form when Petroset-H was used, but both Aquaset II and Aquaset II-H produced final waste forms whose consistency was quite different from the normal clay or concrete. Aquaset II samples hardened like concrete and were powdery on top, particularly at higher agent concentrations. Aquaset II-H samples were crumbly rather than firm and monolithic, most probably due to the production of gypsum from the reaction of sulfate with the calcium in the cement component.

Because it requires no mixing, Aquaset was the agent of choice for large-volume solutions (deionized water, Simple Green) that did not contain significant quantities of neutralization salts, and therefore had a low ionic strength.

In general, when waste volume was sufficient to test the full range of concentrations, the stabilization concentration or concentration range considered "optimum" for each agent coincided with the lower end of the manufacturer's recommended concentration range for low ionic strength solutions and tended to increase as ionic strength increased. (See data, Table II.) Exceptions were the glycerin solution and the uranium oxide, titanium dioxide, salicylic acid mixture. Both wastes required a higher than expected concentration of Aquaset II to achieve a firm final waste form. These data indicate that, when water-soluble organics are present, a higher concentration of stabilization agent may be required.

Only one type of immiscible mixture was stabilized, aqueous salt solutions mixed with the scintillation agent Ultima Gold. Petroset II is required to stabilize the organic layer, and either Aquaset II or Petroset can be used to stabilize the aqueous layer. The Aquaset II/Petroset II combination was used in this study, and resulted in a completely homogeneous final waste form. While it may be necessary when Petroset II is used to add an alcohol to accelerate its setting, none was required for Ultima Gold.

SUMMARY

This treatability study stabilized 51 waste streams with a total pre-treated volume of approximately 130 liters. Waste volume increase with stabilization averaged a factor of 1.5 for all agents, and never exceeded a factor of about 2. Aquaset II and Aquaset II-H worked well for all aqueous wastes except neutralized concentrated sulfuric acid. In order to achieve an acceptable final waste form, aqueous solutions with relatively high ionic strength required larger amounts of Petroset and Petroset-H than the manufacturer's recommended quantities. Aquaset is recommended for dilute aqueous solutions.

No problems were encountered with handling or mixing any of the agents. The earliest stabilized samples (final waste volumes from 100 ml up to 4 liters) have been in storage a little over a year and show no signs of cracking, increased plasticity, or liquid separation.

REFERENCES

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