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SAVANNAH RIVER LABORATORY

Ion Exchange
DWPF
Ion Exchange
Cesium Removal
Waste Supernate

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AN IMPROVED METHOD FOR DECONTAMINATING SOLUBLE HIGH-LEVEL WASTE USING ION EXCHANGE

INTRODUCTION

The tetraphenylborate precipitation (TPB) process was developed to remove cesium from waste supernate because most of the process operations could be carried out in the tank farm area. This eliminated the necessity of constructing expensive buildings required by an ion exchange process that had been considered previously. One of the problems introduced by the TPB process was the severe burden placed on the glass melter and off-gas system in the Defense Waste Processing Facility (DWPF) by the large amount of organic material produced. This necessitated the introduction of a process step in the DWPF to remove much of the organic material before the cesium stream could be sent to the melter. The least expensive method of those considered was precipitate hydrolysis[1], in which the TPB was hydrolyzed with formic acid to yield benzene as the principal organic component. Although about 90% of the organic material can be removed, recent developments have greatly increased the complexity of this step of the process. Other disadvantages of the precipitation process are the relatively large amounts of inert material (Na, K, and Ti) that must be fed to the melter and the hazards and handling problems associated with benzene generated in various steps of the process. It is therefore prudent to consider alternatives to the TPB precipitation process if they can be implemented in a way that achieves the goals of the DWPF project.

A resorcinol-formaldehyde ion exchange resin has been developed recently[2-4] whose cesium capacity was four times greater than the best commercial resin, Duolite® CS-100. The resorcinol resin was found capable of processing about 200 column volumes of simulated and actual high-level waste, containing 5.6 M sodium ion, at 50% breakthrough (the maximum capacity of the resin). This report describes a method by which this resin can be used in a process to replace TPB precipitation. The proposed changes will greatly simplify both the supernate decontamination process and the DWPF processes, and will alleviate most of the problems with respect to operability, materials handling, and safety.

SUMMARY

A resorcinol-formaldehyde cation exchange resin, developed at the Savannah River Laboratory (SRL), can potentially reduce the complexity of the supernate decontamination process in the DWPF flowsheet. Operated efficiently, the resin can effectively remove cesium and then be discharged directly to the melter, producing a durable glass with redox properties as good as or superior to glass prepared with precipitate hydrolysis product. The cesium ion exchange process could possibly be performed by resin columns in the tank farm area; strontium could subsequently be removed with a sodium titanate column. Mercury could be removed with a Duolite® GT-73 column. This might be necessary to prevent saltstone from becoming a RCRA repository. Spent sodium titanate would be sent to the melter with the cesium resin for incorporation in glass. The GT-73 would be rinsed with sodium nitrate to remove cesium and stored for disposal as low-level waste.[6]

When compared with the current precipitation process, an ion exchange process using this resorcinol-formaldehyde resin has the following advantages and disadvantages:

Advantages

- The need for the acid hydrolysis process in the DWPF would be eliminated.
- The amounts of alkali elements going to the melter would be

reduced by a factor of about 8. This would greatly increase the reliability of the glass-making process.

- The amount of titanium going to the melter would be reduced by a factor of about 10. This will significantly reduce the possibility of devitrification in the glass product, and of spinel formation in the melter.
- No boron is introduced to the glass-making process by the spent resin. Thus, boron content in the glass can be controlled by regulating borosilicate glass additions.
- The volume of waste sent to saltstone should be less for the ion exchange process.
- Nitrite additions to control corrosion in precipitate tanks will be eliminated.
- Problems associated with generation of benzene and other organics in the TPB precipitation process would be eliminated.
- The need for a (RCRA) hold tank, incinerator, and mercury removal process to handle the benzene product of acid hydrolysis would be eliminated.

Disadvantages

- The cost and schedule of the tank farm program would be impacted, but not necessarily unacceptably.
- Engineering aspects of the ion exchange process, such as resin transport have not been evaluated in detail. (See p. 11,12).

PROPOSED PROCESS

The supernate would be processed through several resorcinol resin columns in series located in the tank farm area (possibly in a waste tank). When the first column in the series becomes saturated with cesium, the resin would be washed and discharged. The second column would then take the place of the first, the third would take the place of the second and so on. Finally, a column of fresh resin would be placed in the last position. In this manner, near resin saturation can be achieved while obtaining whatever decontamination factor is desired. Figure 1. contains a schematic diagram of this operation.

The supernate would be further decontaminated from strontium and plutonium with a sodium titanate column. The distribution coefficients for these elements were estimated, from data in Reference 5, to be about 1E+05; very little titanate would therefore be required. Mercury would be removed, if necessary, from the decontaminated supernate with Duolite® GT-73 ion exchange columns. About 20% of all the mercury in the waste exists in the supernate, in concentrations of 46 ppm or greater. When incorporated in saltstone, it is probable that the 0.20 ppm RCRA limit for mercury would be exceeded.

The resins containing cesium, strontium and plutonium would ultimately be discharged directly to the melter without further treatment. The question of disposal of GT-73 has already been addressed.[6]

Operating Conditions

Number of Columns:

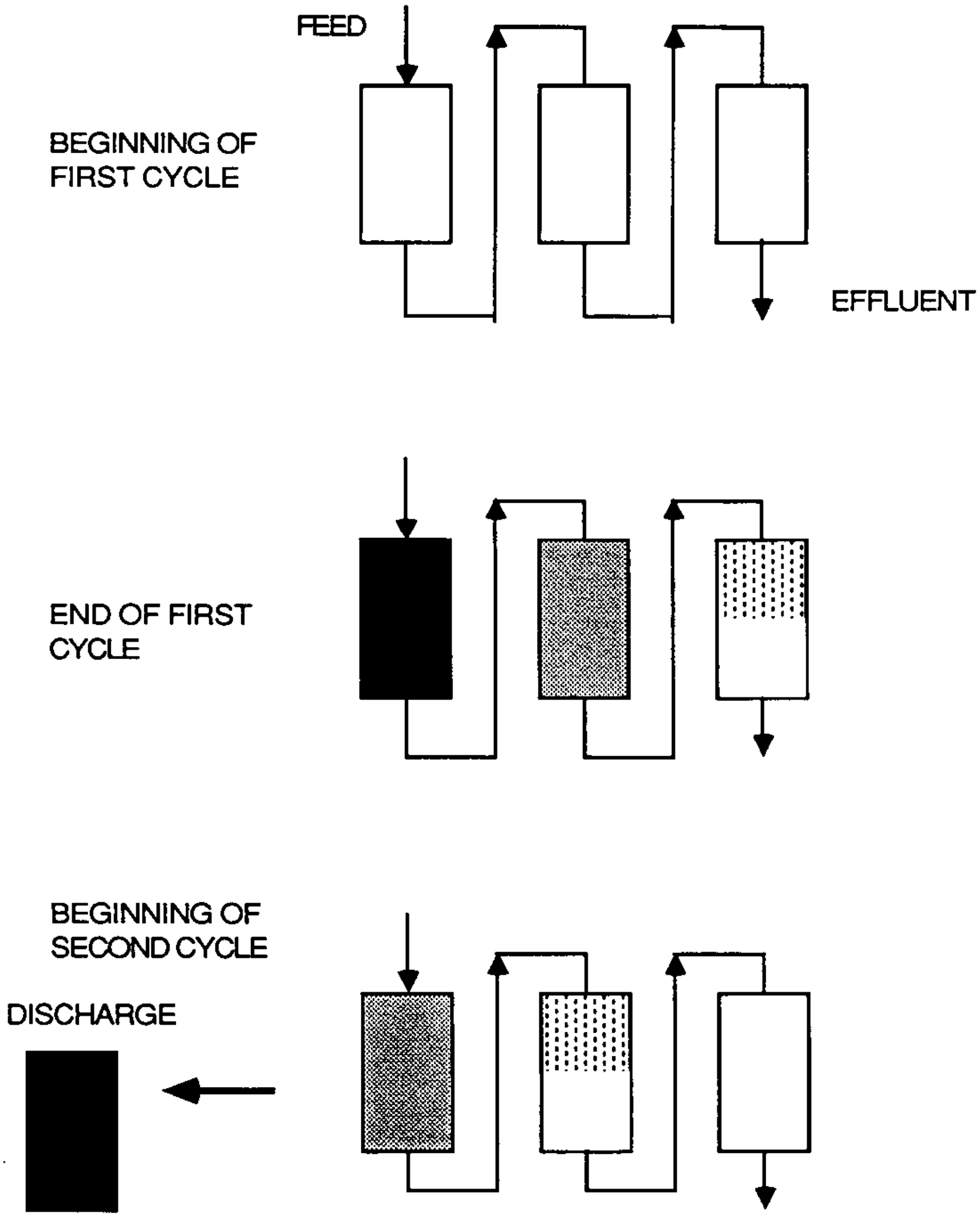
A computer simulation was run to determine the effect on the decontamination factor (DF) of running multiple cycles through the proposed cesium removal process. Figure 2. shows the variation of DF with the number of cycles through the process, for values of N equal to 50 and 100. N is a dimensionless quantity related to the mass transfer coefficient and is defined as follows:

$$N = \frac{Ka\ Kd\ \rho_B}{Cv/hr}$$

where K_a, Kd, and ρ_B are the mass transfer coefficient, the distribution coefficient and the bulk density respectively. The term (Cv/hr) is the specific flow rate of the feed in column volumes per hour. The results show that steady state is approached slowly, but that a DF greater than 1E+05 is obtained after 20 cycles when N = 100. This indicates the proposed process is feasible as long as $N \geq 100$ per column. Similar calculations, with a two column system, showed that a DF of 1E+04 could not be achieved at steady state. A system designed with three columns in series and N = 100 should therefore be adequate. It may be possible to operate with three columns and somewhat smaller value of N, or with two columns if larger values of N can be realized.

Figure 1.

SCHEMATIC DIAGRAM OF ION EXCHANGE SYSTEM



Size of Columns:

With the minimum value of N established it is possible to calculate the minimum size for the columns. The laboratory column run reported in Reference 4. produced an N value of 119 at a flow of 3 Cv/hr. Therefore, that flow should be adequate for use with the present resin. The volume of resin necessary to attain the required production rate can be calculated from the following equation:

$$v = \frac{F}{Cv/hr}$$

where v is the volume of the column in gallons and F is the required flow of the feed solution in gallons per hour. Since the required flow for the present process is 754 GPH, the required volume is 251 gallons or 33.5 ft^3. The resin used in the column test was 40-60 mesh; a finer resin would lead to a larger value of the mass transfer coefficient and hence, to smaller columns.

Cycle Time:

The cycle time is given by the following equation:

$$T = \frac{Cv(50)}{(Cv/hr)}$$

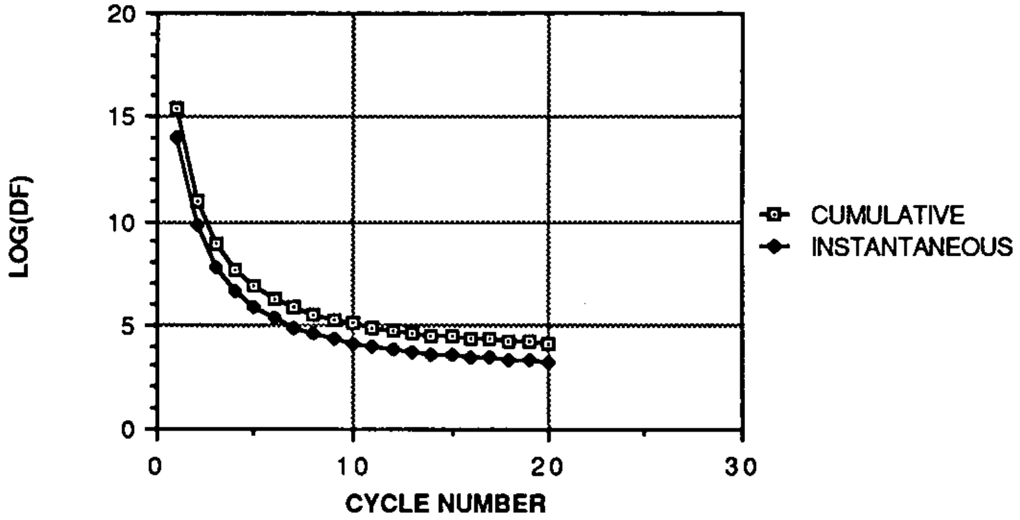
where T is the cycle time in hours, Cv(50) is the number of column volumes to 50% breakthrough. Because Cv(50) = 200 and Cv/hr = 3, T = 67 hr.

IMPACT ON DWPF AND SALT PROCESSING

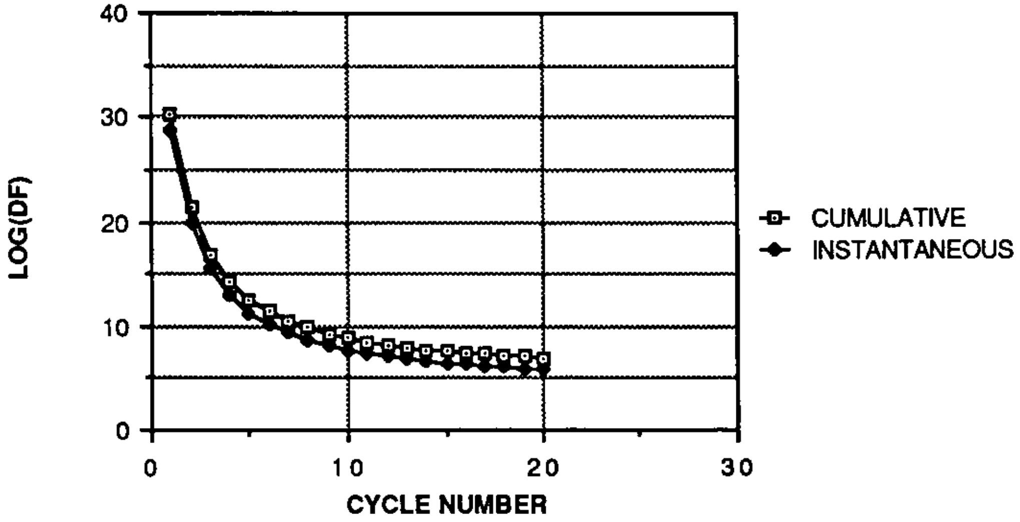
There would be very little impact on the current design of the DWPF except to eliminate the acid hydrolysis step and organic removal sub-steps associated with it. It is conceivable that currently stored precipitate could be blended with spent resin until worked off. The equipment being designed for precipitate hydrolysis would not then have to be installed and tested.

The impact of reducing material (carbon equivalents) on the melter would be about the same as that projected for the TPB process after precipitate hydrolysis. The impact of alkali elements, titanium, and boron on the melter would be much less. A comparison of the amounts of each of these components that would go to the melter from the ion exchange and TPB processes is given in Table 1.

Figure 2.



DF FROM 3 COLUMN SYSTEM, N = 50



DF FROM 3 COLUMN SYSTEM, N = 100

Table 1.

FLOW TO DWPF FROM TPB AND RESIN PROCESSES

COMPONENT	TPB PRECIPITATION	RESIN PROCESS
Salt Flow, GPH	754.3	754.3
TPB (all types), lb/hr	47.03	-
Resin, lb/hr	-	11.32
Carbon Equiv, lb/hr (a)	4.73 (c)	5.49
Carbon Equiv, lb/hr (b)	5.68 (c)	5.78
Potassium, lb/hr	5.63	0.63 (d)
Sodium lb/hr,	2.43	0.37 (d)
Total Alkali, lb moles/hr	0.249	0.032
Titanium, lb/hr	0.849	0.063
Boron, lb/hr	1.53	0.00

(a) CO_2 Basis
(b) CO Basis
(c) This represents carbon equivalents going to melter; the value assumes 90% by precipitate is destroyed by hydrolysis.
(d) Assumes 50-50 split of Na and K on resin

The impact on salt processing would be somewhat more severe. The ion exchange columns might be installed in the risers of an existing waste tank; otherwise, a shielded facility in the tank farm would have to be identified or constructed to accommodate them. A method for storage of the saturated resin before the DWPF is ready to begin processing, would have to be developed. Both would have to be accomplished in time to keep the tank farm on schedule.

Total Resin Flow: The total resin flow to the melter was found to be 11.32 lb/hr, based on the assumption that 200 column volumes of dissolved salt solution could be processed by the resin, the bulk density of the resin is 0.36 g/ml (3.00 lb/gal), and the salt processing rate is 754 gal/hr. While variability in the sodium and cesium ion concentrations in the feed in this process is recognized, column data suggest that 200 column volumes is a reasonable estimate[4].

Reducing Agents: The total flow of reducing material to the melter from the ion exchange process, expressed as carbon equivalents, is 5.49 to 5.78 lb/hr compared with 4.74 to 5.68 lb/hr for the precipitation process after 90% of the organic has been removed by the precipitate hydrolysis process. The range of values arises from assuming different products of combustion, as described below.

The total flow of TPB to the DWPF was calculated from the most recent flow sheet data[7] and summarized in Table 7. Carbon equivalents were calculated assuming hydrogen is converted to H_2O, alkali elements to their respective oxides, boron to B_2O_3, and carbon either to CO or CO_2. Two formulas for calculating carbon equivalents result from these assumptions.

$$Ceq = 12(n_C + 1/4\ (n_H + n_K + n_{Na}) + 3/4\ n_B - 1/2\ n_O); \quad (CO_2 \text{ Basis})$$
$$Ceq = 12(n_C + 1/2\ (n_H + n_K + n_{Na}) + 3/2\ n_B - n_O); \quad (CO \text{ Basis})$$

where n_i = the number of atoms, of an element in the formula of a compound; i represents the symbol of the element.

The Ceq of one gram formula weight (357.9 g) of potassium tetraphenylborate ($C_{24}H_{20}B\ K$) is 360 (CO_2 basis) or 432 (CO basis). The Ceq of one gram of KTPB is therefore 1.006 or 1.207 (g carbon/ g KTPB)

The Ceq per 100 g of the resin was calculated from the analytical data given in Table 1. using a modification of the above equation as follows:

$$Ceq = \%C + 3(\%H) + 3/23(\%Na) + 3/39.1(\%K) - 3/8(\%O); \quad (CO_2 \text{ Basis})$$
$$Ceq = \%C + 6(\%H) + 6/23(\%Na) + 6/39.1(\%K) - 3/4(\%O); \quad (CO \text{ Basis})$$

from which the Ceq of one gram of resin was calculated to be 0.485 (CO_2 basis) or 0.511 (CO basis) (g carbon/g resin).

The above considerations indicate that resin would have about the same effect on the redox behavior of the glass as KTPB. The only way to be assured that the resin will not adversely effect the glass, however, is to determine it experimentally. Resin will be fed to the glass melter at a rate of 11.32 lb/hr. The rate of glass production in the DWPF will be 228 lb/hr. Therefore, the ratio of resin to glass will be 0.050. C. M. Jantzen has run tests in which resorcinol resin was added in the preparation of sludge-only glass in the amounts of: 0.02, 0.07, and 0.14 grams of resin per gram of glass. The two lower concentrations of resin produced glass with properties comparable to those of sludge-only glass. Her work will be reported elsewhere.[8] It appears, from these tests, that the glass melter can tolerate substantially more resin than would be delivered by the process.

Alkali Elements: The flow of alkali elements to the DWPF from the resin process, shown in Table 1, was estimated from the analytical data given in Reference 4, and the resin flow. An alkali flow of 0.032 lb moles/hr was calculated; the split between sodium and potassium is uncertain at this time. The flow of alkali from the precipitation process, also shown in Table 1, was estimated, from data in Table 2, to be 0.249 lb moles/hr. About 8 times more alkali is fed to the melter by the precipitation process than the resin process. This requires removal of alkali from the frit in order to produce an acceptable glass. Thus, the consequences (to the DWPF) of process upsets such as batching errors are potentially much more severe for the precipitation process as compared with the ion exchange process.

Titanium: The flow of titanium from the resin process was estimated to be about 0.063 lb/hr, based on the assumptions that an efficient column of sodium titanate would be used and that the distribution coefficient for strontium and plutonium would be about 100,000. This value is considerably less than the 0.849 lb/hr produced by the precipitation process. Reducing the Ti content of the melter feed would diminish the possibility of devitrification, either in the glass product or in the melter during processing.

IMPACT ON SALTSTONE

In the precipitation process, a large amount of corrosion-inhibited wash water is required that ultimately will go to saltstone. Very little wash water would be needed in the ion exchange process, hence less saltstone would be produced. The composition of the saltstone should not be changed greatly.

Table 2.

FLOWS TO DWPF FROM TPB PROCESS

COMPOUND	POUNDS PER HOUR	POUND MOLES PER HOUR
KOH	1.12	2.16E-02
KTPB	43.80	1.22E-01
NaTPB	0.15	4.39E-04
NH_4TPB	2.50	7.42E-03
CsTPB	0.58	1.28E-03
$NaNO_2$	5.49	7.96E-02
$NaNO_3$	0.15	1.76E-03
NaOH	0.25	6.25E-03
$NaHTi_2O_5$	1.77	8.86E-03
Na_2CO_3	0.13	1.23E-03
$Na_2C_2O_4$	0.11	8.21E-04
$Na_2B_4O_7$	0.50	2.49E-03

ISSUES TO BE ADDRESSED

There are several issues remaining that must be addressed concerning the resin process. These include:

- o Will a full-scale plant test reproduce the laboratory data?
- o At what radiation dose does the matrix of the resin begin to lose its integrity?
- o What chemical species are generated by radiolytic destruction of the resin and will they require special handling and safety precautions?
- o Is space, such as the filter building, currently available to house the ion exchange process, or will additional space be needed ?
- o What equipment will be needed?
- o Can spent resin be pumped?
- o What is the maximum amount of spent resin that can be

incorporated into glass?

- Can a resin, that will meet performance specifications, be obtained in sufficient quantities to maintain the current schedules for saltstone and the DWPF?
- Can the resin be manufactured by several reputable vendors?

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