ALTERNATIVE TREATMENT OF MEDIUM LEVEL LIQUID WASTE BY CHEMICAL PRECIPITATION AND SLUDGE VITRIFICATION

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ABSTRACT

The adaptibility of the FIPS-process - originally developed for the solidification of highly radioactive fission product solutions - as an alternative method of treatment of medium level liquid waste will be investigated. The proposed alternative to the current practice is the separation of the crucial radionuclides from the bulk of low active liquid by chemical precipitation, followed by the vitrification of the sludge. The remaining low active waste can be incorporated into bitumen or concrete. The low activity of these products would allow handling without additional shielding or at least, with a considerable reduction of the shielding.

BACKGROUND AND MOTIVATION

In a reprocessing plant considerable amounts of medium active liquid wastes (MAW) will be generated. According to the current practice of waste treatment, the MAW will be concentrated, then incorporated into Bitumen or concrete for a final disposal. As the self shielding of the solidified products is not sufficient, additional shielding is necessary to meet the required limits for dose rates during handling and transportation. The total weight to be transported is therefore many times higher than that of the radioactive product. This causes the transportation costs to rise and demands large storage capacity if the additional shielding mentioned above is used.

Calculating on the basis of 350 t heavy metal to be reprocessed per year (the actual throughput for a German reprocessing plant under design), the amount of medium activ liquid waste (MAW) generated in the PUREX process will approximately be 1500 m^3 per year after being concentrated. The concentrate contains 1 - 1.5 mol/l nitric acid and 350 g/l salts, mainly sodium nitrate. The total activity amounts to some 10^7 GBq according to 40,000 MWd burn-up and 7-year cooling time.

Depending on the strategy of waste conditioning, the expense of shielding differs. Choosing cementation in 400 l drums, the weight of the product would reach about 5500 t/year, and an additional concrete shielding of 38,000 t would be necessary. From this point of view bituminization would be more economical because it produces about 1000 t/year bituminized waste in 200 l drums which can be shielded with 21,500 t of concrete. In both cases it would be worthwhile to separate up the MAW into a small highly radioactive fraction containing the bulk of radioactivity which must be vitrified and a large fraction of low active liquid waste (LAW), as it has already been suggested[1].

The LAW should be bituminized or cemented; its activity level would allow handling and transportation without additional shielding.

Chemical precipitation and subsequent separation of the radionuclides followed by their solidification appears to be a suitable method to achieve the aspired effect.

The Institut für Chemische Technologie der Nuclearen Entsorgung in the Kernforschungsanlage Jülich has proposed to adapt the FIPS-process[2], which has originally been developed for the solidification of highly radioactive fission product solutions, as a suitable technique for this alternative treatment of MAW.

CURRENT PROGRAM

General

The research underway and development program covers the whole procedure of fractioning the MAW and vitrification of the highly radioactive fraction.

The work is carried out as a part of a joint 5-year program for the treatment and the disposal of radioactive wastes supported by the Commission of the European Communities.

The proposed process consists of:

i denitration of the MAW concentrate,
ii chemical precipitation of the radionuclides,
iii separation of the sludge,
iv mixing with glass powder,
v drying on a drum drier and
vi melting.

Chemical precipitation and separation of the sludge had to be integrated into the original FIPS flow sheet (Fig. 1).

Considering that the process has to be carried out remotely controlled in a hot cell, the development goal is a simple process which is insensitive to narrow parameter ranges. This requirement might be in conflict with the necessity of accurate pH control for effective precipitation.

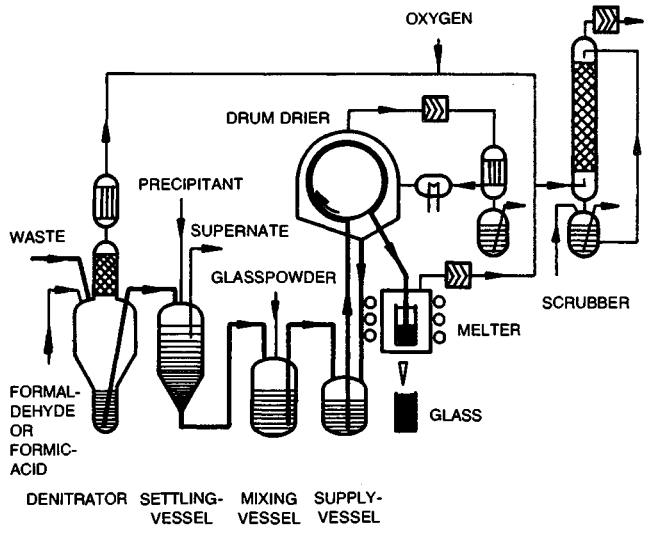

Fig. 1. Flow Sheet for the Treatment of Medium Level Liquid Waste by Separation and Solidification of Radionuclides.

Denitration

Neutralization of the nitric acid with sodium hydroxide would increase the amount of salt to be solidified by 170 t/year. Therefore preference has been given to the denitration with formaldehyde or formic acid, producing NO_x by this means which partly will be released as N_2O and partly recombined to nitric acid by scrubbing with water. Feeding the MAW into the preheated formaldehyde or formic acid batch will yield more N_2O than the reverse (Fig. 2). This is an advantage if nitric acid should not be recovered. However, on account of simple process control in the FIPS-process the feeding of the reducing agents into the heated MAW will be prefered.

In the hot cell apparatus FIPS-II 10 l batches can be denitrated. The work was started with simulated MAW concentrate, the composition which is shown in table I. It contains the fission products as well as sodium nitrate and complexing agents from decontamination. In order to simplify the approach, only the fission products and the sodium nitrate have been considered first. Denitration had to be carried out with reflux due to the high salt content of the solution.

The following steps of precipitation require accurate adjustment of the pH value to optimize the decontamination factors for the above mentioned nuclides. The recomended pH value for precipitation of cesium is 4 which corresponds to a pH value at the end of the denitration with formaldehyde ranging between 3 and 4. Using formic acid, the pH values vary between 2 and 3 depending on the residual formic acid content.

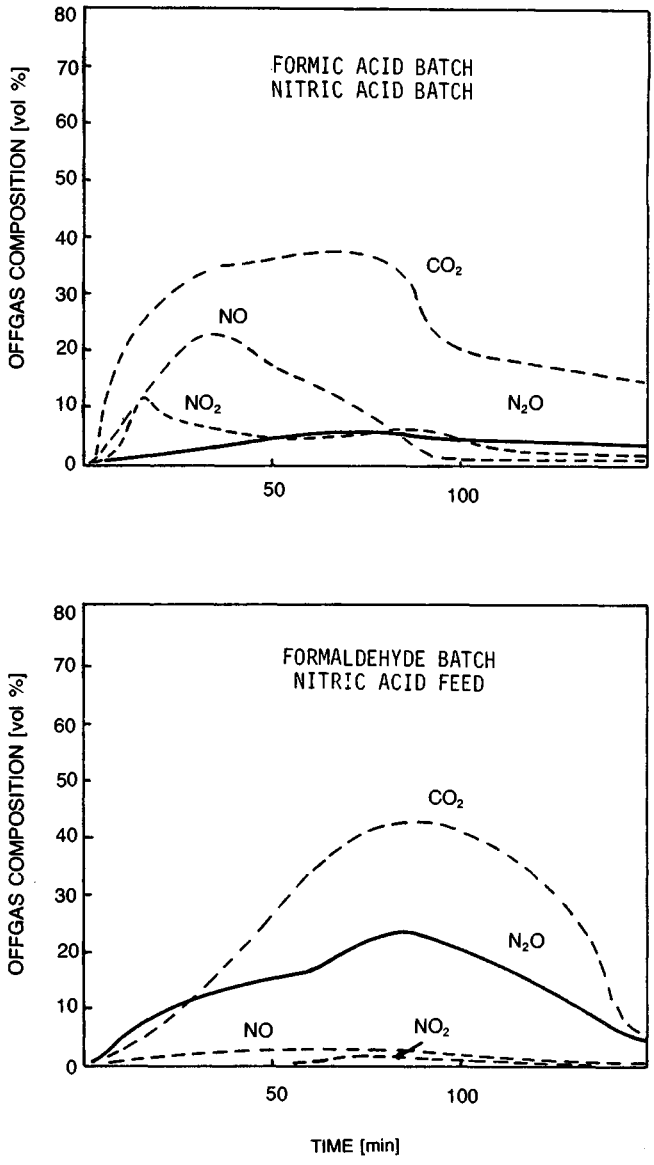

Fig. 2. Composition of the Offgas During Denitration.

Table I. Composition of the Simulated MAW.

Element Compound	g/l	Element Compound	g/l
$NaNO_3$	300	Mn	0.08
Al	0.23	Mo	0.38
Ca	1.5	Ni	0.08
Cr	0.08	Ru	0.15
Cu	0.15	Zn	0.15
Fe	0.38	Zr	0.08
K	0.08	Cs	0.3 (10)[a]
Mg	0.75	Sr	0.3 (10)
Na-oxalate	5	Marlox FK 64	1
Na-tartrate	5	Marlophen 812	1
Na-citrate	5	TBP	0.2
EDTA	1	DBP	0.2
NaF	1	Kerosin	0.02
Na_2HPO_4	5		

[a]For non active Experiments

Precipitation

The dose rate of 10 m rem/h at 1 m distance from the surface of the drums is the licencing requirement for the shielding. The required decontamination factors are, in case of cementation, 280 for cesium, 12 for antimony and 6 for ruthenium, and, in the case of bituminization, they are 900 for cesium, 40 for antimony, 15 for ruthenium, 5 for cobalt and 5 for europium.

For the present only cementation is taken into consideration. In order to investigate whether the precipitation step could be simplified (taking into account that it must be done with real waste on a large scale in a future plant), laboratory experiments were initiated with one-step precipitation. Experimental work had to be concentrated on cesium, being the crucial element. Antimony and ruthenium are of minor importance as the decontamination factors required for them are comparatively low and are expected to be achieved even under unfavourable conditions without extensive additional treatment.

The experiments have been performed batchwise with 200 ml MAW solution containing 10 g Cs/l. A preformed precipitate of $K_4[Fe(CN)_6]$ and equimolar $Ni(NO_3)_2$, which is thought to be $Ni\ K_2[Fe(CN)_6]$, is added to the solution at a pH of 3 - 4 after denitration at a molar ratio of 3,5 mol precipitant to 1 mol cesium. The pH is then increased to 9 by addition of sodium hydroxide. The solution will not be filtered; samples are taken from the supernate after the sludge has settled.

Preliminary results show a decontamination factor of 100. By comparing this with the required value, it is clear that further optimization of the precipitation is necessary. More realistic experiments with a cesium content of 0.3 g/l using Cs 134 as tracer are under way.

The decontamination factors for ruthenium and antimony were found to be 2 - 5 by the above methode. Therefore, it is anticipated that the required values of 6 and 12, respectively, can be achieved by adding proper precipitants even without accurate pH adjustment.

Separation

Centrifugation and filtration are common methods for the separation of the sludge from the supernate. The use of filters under hot conditions at full scale may be a problem. Therefore it will be investigated whether the application of the FIPS-process, especially when mixing the sludge with glass powder before drying on the drum drier, can eliminate filtering.

Considering the large amount of MAW to be treated, precipitation and sludge separation should work continuously. Quick sedimentation is desirable to minimize equipment size. Its achievement has therefore emphasized. The influence of the pH value and the addition of glass powder on the settling rate has been investigated.

Figure 3 shows the effect of the pH adjusted to 7, 8 and 9, respectively, after the addition of the precipitant. Rising pH will slow down sedimentation. This tendency is also observed if glass powder is mixed into the solution as shown below. It should be pointed out, that average values are plotted. The results of nearly all series of experiments fluctuate, indicating sensitivity to even minor changes of the process parameters.

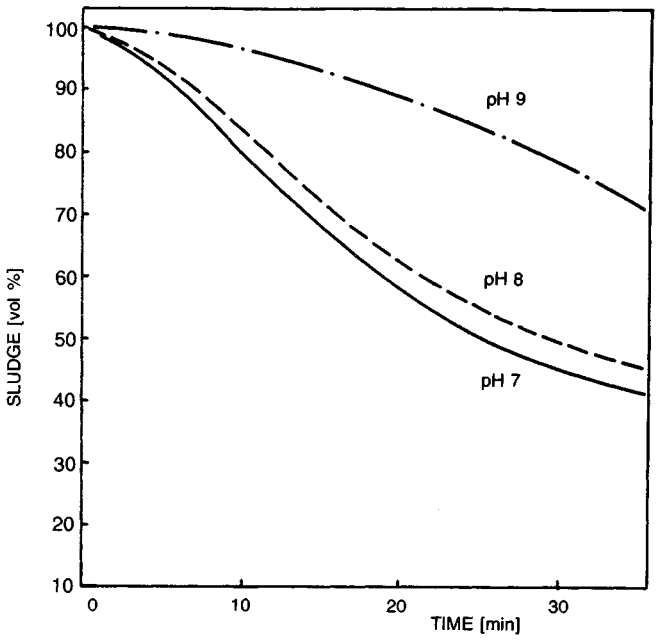

Fig. 3. The Effect of the pH Value on the Settling Rate.

Figure 4 shows that the settling time can be reduced dramatically by adding glass powder to the solution. The minimum settling time can be achieved by adding the 60 µm powder before the precipitating agent and sodiumhydroxide. In all cases 10 g glass powder was mixed into 200 ml solution and the final pH was adjusted to 8.5. Further experiments with varying amounts of glass powder between 5 g and 20 g did not show significant differences.

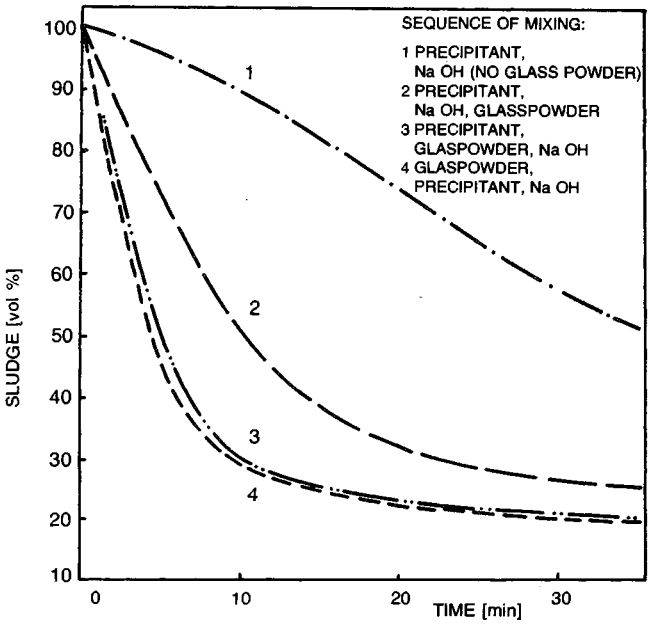

Fig. 4. The Effect of the Addition of Glass Powder on the Settling Rate.

Solidification

The water content of the suspension to be dried on the drum should range between 60 % and 70 %. Therefore, the liquid content of the sludge discharged from the settling vessel can be relatively high. Figure 4 shows that the volume of the sludge can be reduced to about

25 % of the initial volume in an acceptable time.

Assuming that the sodiumnitrate concentration does not change and the major amount of the waste is concentrated in the sludge. 27 g sodiumoxide and about 6 g waste oxides have to be vitrified per liter MAW, considering the more realistic value of 0.3 g Cs/l instead of 10 g/l. Due to the high sodium content of the sludge, which is assumed to be the limiting factor for the incorporation of the waste into the glass, the sodium oxide content of the matrix glass must accordingly be reduced.

The calculated value of 27 g sodium oxide in the sludge per liter MAW results in 25 % sodium oxide in the glass (Table II) which corresponds to the upper limits for sodium content in commercial glasses. The waste oxide content consequently amounts to 5.5 % as shown in table II. During future development the composition of the waste to be vitrified will become more complicated, therefore, the comparatively low waste content should be regarded as a margin of safety.

Table II. Approach for Glass Composition

Compound	Referring to Sludge per Liter MAW	Glass Composition
Na_2O	27 g	25 %
Wasteoxides	6 g	5.5 %
Glass	75 g	69.5 %

FUTURE WORK

Future work will investigate each step further. The research will be done on two different scales in parallel: one using 100 - 200 ml batches for cold laboratory experiments and the other using 10 l of MAW in the adapted hot cell apparatus FIPS-II. By this means it should be possible to clarify whether or not the data obtained under favorable laboratory conditions are reproducible under remote handling in a hot cell using real wastes and whether or not there are other factors to be considered for further research.

REFERENCES

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2. S. Dix, St. Halaszovich, V. Mirschinka, Fission Product Solidification: FIPS. JOL-Conf-42 (1981) Vol. I, pp. 35-51