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MEMORANDUM

October 9, 1985

TO: E. L. ALBENESIUS, 773-A

FROM: D. F. BICKFORD, C. M. JANTZEN, 773-A
DFB CMJ

FOREIGN TRAVEL REPORT
WEST GERMANY AND BELGIUM
SEPTEMBER 9 - SEPTEMBER 13, 1985

INTRODUCTION AND SUMMARY

On September 16 to September 18, 1985 we visited Kernforschungszentrum, Karlsrule, West Germany. On September 19 and 20, D. F. Bickford visited the PAMELA Plant in Mol, Belgium. The purposes of these visits were:

1. Presentations at the Karlsrule KfK Workshop on SRL's experience with the chemistry of vitrification and waste form performance.

2. Identification of common interests and problems in waste glass vitrification.

3. Identification of areas of concern to be discussed at future FRG-USA Workshops.

4. Consultation on melter material performance at the PAMELA Plant in Mol, Belgium.

Participation in the KfK workshop served to enhance FRG-USA expertise relative to the safe vitrification of HLLW. Areas which were technologically solved and areas which required further study were identified. Waste glass chemistry, glass physical property control by frit optimization, cold cap chemistry, the role of melt insolubles, the role of Tc and Ru, glass redox, offgas corrosion, laboratory scale melter studies and waste glass durability modeling were among the topics discussed. The general consensus was that the technology to safely vitrify HLLW exists with some problem areas to be examined further and discussed at future FRG-USA workshops.

Visitation of the PAMELA plant provided an opportunity to observe the operation and design of this European waste solidification facility.

Karlsruhe Workshop on the Chemistry of Vitrification

A FRG-USA Workshop on the Chemistry of HLLW Vitrification was held at KfK-INE, Karlsruhe (September 16 - 17, 1985). There were over 20 attendees from the following affiliations:

KfK, KfA, WAK and HMI in FRG
DWK in Belgium
DOE-HQ, DOE-WV, SRL, Idaho Falls, PNL and RHO in USA

The individual attendees are listed in Table I.

The aim of the workshop was to exchange expertise relative to the safe vitrification of HLLW in order to determine which areas were technologically solved and which areas required further study. Among the topics discussed were waste-glass chemistry, glass physical property control by frit optimization, the cold cap chemistry, the role of melt insolubles, role of Tc and Ru, glass redox, offgas corrosion, laboratory scale melter studies and waste glass durability modeling. Overall, the participants learned about the diversity of HLLW that borosilicate glass vitrification can accomodate when the processing and glass chemistry are adjusted accordingly. The common interests and problems were identified. The general consensus was that the technology to safely vitrify HLLW exists with some problem areas such as the melt chemistry of Tc, Se and noble metals under varying redox conditions to be examined further (details are given below). Areas of concern to be discussed at future FRG-USA workshops were the following:

- o progress made in waste vitrification in ongoing problems
- o progress made in the behavior of radioactive waste in melters, both laboratory and full scale

- o long term corrosion of borosilicate glass and canister materials
- o repository relevant corrosion of waste package components
- o behavior of radioactive waste glass in repository relevant conditions, e.g. behavior of Pu

A short compilation of the minutes will be distributed to the participants in order to initiate specific cooperation and future interactions.

In detail, the presentations by Horst Pentinghaus, the meeting coordinator at KfK, concentrated on German experience in vitrification of simulated commercial HLW, with a nitric acid flowsheet. The Germans feel that they have adequate frit formulations to vitrify 11 w/o loaded borosilicate glass. The difficulties which limit the waste loadings include:

- o limited solubility of rare earths in glass
- o formation of metastable "yellow phases" composed of 12% Na_2O, 9% Li_2O, 30% SO_3, and 10% MoO_3
- o alloying of insoluble Pd, Rh, and Ru with Te to form low melting analogs to sulfides (in one run the alloying resulted in a 4 cm thick layer on the bottom of the melter)

Their approach to handling these problems is a combination of adjustment of frit composition and limitation of melter residence times to avoid exsolution. With bottom draining of the melter they do not expect accumulations of precious metals in the melter.

The US participants, William J. Bjorklund, Dennis F. Bickford and Bruce Staples, discussed the wide ranges of HLLW chemistry in the US while Bruce Staples and Carol M. Jantzen discussed the optimization of borosilicate frit compositions to achieve desired glass physical properties, as well as glass performance in repository relevant environments.

The FRG melt chemistry is dominated by the need to destroy or volatilize the 5M nitric acid in the feed. They postulate that this results in extensive molten salt reactions during the melting process. This would appear to be aggravated by their use of relatively large (~1mm diameter) glass balls as feed rather than ground frit. Work done by Odoj of KfA, Julich indicates that 80% of their Tc will volatilize unless they change to reducing melt conditions. Apparently they will not add reducing agents until it becomes unavoidable.

Dennis F. Bickford presented the defense waste vitrification experience with reducing melts. Limits have been established for the prevention of nickel sulfide formation. Redox control regulates sulfur solubility, metal formation and foaming. Both PNL and SRL results indicated that precipitation of noble metals is controlled by both redox and agglomeration. However, differences in the feed stream chemistry at SRL, PNL, and WV dictate different approaches to redox control.

KfK processing and experience is more directly applicable to West Valley and potential commercial reprocessing waste than to DWPF. Concentrations of difficult to manage fission products (Pt, Pd, Ru, Se, Te, Tc) are orders of magnitude higher than in DWPF waste, so there is a tendency to believe that if KfK does not experience problems with these fission products, then neither will DWPF. Probably the largest potential exception to this, however, is with respect to the formation of sulfide analogs from noble metals, Se and Te. The more reducing conditions of the DWPF melter will tend to increase the likelihood of aggregation and precipitation of these electrically conductive phases in the melter. At the same time, routine bottom draining is not planned in the DWPF which may permit accumulations.

KfK is relying on the leach testing and modelling being carried out at Hahn-Meitner Institut, Berlin. Werner Lutze presented the HMI leach model which assumes that the glass can continue to alter after the solution concentrations reach solubility limits for the glass matrix elements and that, therefore, a long term dissolution rate is applicable and can cause significant alteration of glass despite the leachate reaching saturation. In particular they model the long term dissolution rate as having a linear time dependence, t^1, as this is the time dependence for alteration layers (palagonite) to form on basalt glass. They calculate 30% alteration of a glass cylinder of 0.5m by 0.17m radius at 200°C in 100 years. However, they then assume a linear dependence of the formation of alteration layers in the cracks of natural glasses and apply this to waste glass which has fractured during cooling. By assuming that the entire waste glass surface area after fracturing (a factor of 10X increase) is available for long term leaching, and taking no credit for the effects of silica saturation or gel layer formation in the microenviroment of a crack, they maintain that fracturing of the waste glass will adversely effect waste glass durability so that after 100 years at 200°C there will be 100% alteration of the proposed glass cylinder. These calculations are based on several assumptions; linear dependence, no surface layer formation, a factor of 10X increase in surface area, and a relatively small cylindrical block size. The SRL and Japanese large scale leach test results show that waste glass durability is only decreased a factor of 2-3X due to fracturing. These results were presented by Dennis F. Bickford.

The HMI model is only used for glasses which dissolve by similar mechanisms, e.g. waste glasses and natural basaltic glasses, but the benefical effects of low temperature, low pH and high silica concentration of the leachant (simulated groundwater) to retard glass corrosion are numerous. The use of natural analogs is similar to the approach at SRL where hydration thermodynamics is used to model the relative performance of a wide variety of ancient and natural glasses. This approach applies to glasses which leach by different mechanisms. Thermodynamics and bond energetics are empirically correlated and related to silica release to the solution. Bond energetics and thermodynamics are also correlated with gel layer compositions, leaching mechanisms and surface layer formation. The SRL model was presented by Carol M. Jantzen.

Final discussions centered around experiences with laboratory scale melters and modelling, and the characterization of waste glass canister contents. During the final summary session the general consensus was that the technology to safely vitrify HLLW exists, with some problem areas to be examined further. Areas of concern to be discussed at future FRG-USA workshops were identified as outlined above.

PAMELA Visitation in Mol, Belgium

On September 19, 1985 the attendees listed in Table 2 met at Project PAMELA in Mol, Belgium. PAMELA started hot operations on August 29, 1985, with 800 Ci, and will be operated continuously until October 1, 1985, when it will shut down for final licensing. Total cost was $53,000,000 excluding R&D at Karlsruhe. Total operating staff is 55, including maintenance and OHP, with Horst Wiese as OTM and OHP manager. A separate project group is engineering the changes necessary for the start of vitrification in 1988 of the 600 m^3 of High Enrichment Waste Concentrate (HEWC) at Eurochemic. For HEWC, other processes (e.g. French AVM) have not been ruled out. Eurochemic is currently paying $6,000,000/year for LAW immobilization at PAMELA. Four melter campaigns of five weeks duration each will vitrify the LAW. The total will be 400 canisters of borsilicate glass, and 400 canisters of glass beads in lead. An SRL engineer will be permitted to monitor the second LAW run, about the second week of June 1986 as part of US/FRG Cooperative Exchanges. Horst Wiese and Dr. Heimerl (head of analytical development and operations) are anticipating visiting SRL/SRP in the spring.

Operations Flowsheet and Tour

The operating flowsheet was reviewed prior to the tour. Details of this, and the equipment are available in DPST-85-773 (Trip Report, R. E. Edwards and J. R. Glasscock). Observations and recent results:

- Pouring is currently controlled by weight, with 30 cm freeboard. In order to assure accurate weights, a gap was permitted between the canister and the bottom tap mechanism. In the third pour this resulted in air deflecting the glass stream, the glass froze in place plugging the mechanism, requiring a cell entry to correct it.

- The bottom drain valve looked very rugged and relatively easy to change remotely.

- Glass samples are being obtained from the frozen glass fibers that are always found between the filter canister and the pour spout. These are being used for mass balances, but not for glass quality assurance.

- Every 150 to 200 operating hours the dust scrubber and off gas line are cleaned by a reamer on the end of an electrically operated device similar to a plumber's snake.

- Recycle to the melter from the dust scrubber is about 10% of the melter feed rate.

- Canisters are being ultrasonically deconned for 50 minutes and rinsed. They may have substantial problems with this method if their melt cell becomes highly contaminated.

- Their automatic canister welder was demonstrated. It used 4 tack welds, and a final weld. Inspection is only visual, with weld parameter recording. A pressurized soap bubble test is considered sufficient for leak checking. Only one canister in 50 is destructively examined. 300 canisters have been welded without rejectable defects. The welder head is about 2 ft. in diameter by 3 ft. high.

- Two independent electronic control and alarm systems are used to operate feed preparation, melter and off gas systems. Plotting for analysis is rapid, but data is lost after 35 hours.

- Inoperable melters will be broken down and put into 50 gallon drums for disposal. This process could become very difficult if the disassembly cell becomes highly contaminated.

- Radioactive dopants have been feed to the PAMELA melter system to verify off gas scrubbing efficiencies for licensing. Overall efficiencies have exceeded design requirements. PAMELA personnel are expecting final licensing in October. Experimental DF's are shown in Table 3.

SULFIDATION OF INCONEL 690

On September 18 & 20, D. F. Bickford met with Dr. S. Weisenburger and Dr. H. Wiese, respectively, to discuss sulfidation of Inconel 690 in the K-3 melter. Discussions included visual examination of the off gas, melter feed tube and air lift penetrations, review of a Brown-Boveri Co. (B-B Co.) report examining the off gas line failure, and SRL studies of the sulfidation process. SRL conclusions include the following:

- Sulfidation resulted when sulfate and fluoride salts deposited on the inside of a horizontal section of the I690 offgas pipe. The pipe was normally at a temperature too low for sulfidation (~350°C) but portions of it have exceeded 850° during idling.

- The KfK use of ~1 mm diameter glass beads in lieu of powdered glass frit contributed to the attack. There was not evidence of frit splatter or entrainment in the pipes. Thus, there would not be any reduction in sulfide activity in deposits by dissolution in glass, and the offgas pipe was probably subjected to concentrated mixtures of sulfate and fluoride salts. The sulfur content of offgas deposits was measured and found to be high. As a result of the visit, KfK is analyzing the deposits for chloride and fluoride.

- The plasma spray coat recommended by B-B Co. is a reasonable approach for PAMELA, but is not applicable to DWPF. PAMELA will run with low plenum temperatures, with no lid heat. Flaws in the coating will probably cause them little concern particularly if they maintain low plenum temperatures during melter idling. Thermal cycling during DWPF operations with higher plenum temperatures makes these coatings unattractive.

- Recent tests at SRL indicate that I671 is more sulfidation resistant than I690 and should be considered as a back-up material. Samples of the alloy were given to Dr. Weisenburger for exposure tests.

EUROCHEMIC HEWC - POTENTIAL USE OF SRL MERCURY STRIPPING METHODS

On September 20, 1985, D. F. Bickford met with Dr. Eschrich, General Manager of Eurochemic, Mol, Belgium. Eurochemic has 600 cubic meters of High Enrichment Waste Concentrate (HEWC) containing mercury and 10 Ci/liter activity in 0.5 M nitric acid solution. The waste contains <0.04 molar sulfate and <0.04 molar fluoride, 54 g/l Al and 2 g/l Fe. Eurochemic must immobilize the waste for 50 year storage prior to final disposal by Belgium.

Dr. Eschrich is responsible for recommending the final processing method for the waste, and has been particularly concerned with the 2 g/l mercury content. He was considering denitration with formaldehyde, with Hg precipitation. The general SRL programs on ion exchange methods for Hg removal were described to him. He was very interested in considering this as an alternative feed preparation process and requested copies of SRL reports detailing the tests.

DFB/CMJ:msm

#14

TABLE 1: Attendees at Karlsruhe Workshop on the Chemistry of HLLW Vitrification

Name	Affiliation	Telephone
Dennis F. Bickford	Savannah River Laboratory	803-725-3737
William J. Brumley	US DOE/Savannah River	803-725-3296
William J. Bjorklund	Battelle Pacific NW Laboratory	509-376-5674
Amal De	DWK/Mol (Belgium)	014-312861
Lorenz Finsterwalder	WAK/BG	07247-88-416
William H. Hannum	US DOE/West Valley	716-942-4312
Edward J. Hennelly	Savannah River Laboratory	803-725-5323
Carol M. Jantzen	Savannah River Laboratory	803-725-2374
Lothar Kahl	KfK/INE	07247-824397
Manford Kelm	KfK/INE	07247-822676
Karl-Dieter Kuhn	WAK/BG	07247-88-453
Berthold Luckscheiter	WAK/BG	07247-88-462
Werner Lutze	Hahn Meitner, Berlin	030-80092219
Jack L. McElroy	Battelle Pacific NW Laboratory	509-375-2532
Reinhard Odoj	KfA/Julich	02461-616190
Horst Pentinghaus	KfK/INE	07247-824476
Erich Schneider	KfK/PWA/PL	07247-824866
Bruce Staples	Westinghouse Idaho Nuclear	208-526-3449
Ray D. Walton, Jr.	US DOE/Headquaters	301-353-3388
Donald D. Wodrich	Rockwell Hanford Operations	509-373-2038

TABLE 2: Attendees at Mol, Belgium

Name	Organization	Telephone
✓Denny Bickford	SRL	803-725-3737
Don Wodrich	Rockwell Hanford	509-373-2038
Ray Walton	US DOE HQ	301-353-3388
✓William J. Brumley	US DOE-SR DWPF	803-725-3296
✓Edward Hennelly	SRL	803-725-5323
Horst Wiese	DWK	14-240-400
Dr. Heimerl	KfK/EC	N/A
William Hannum	US-DOE (West Valley)	716-942-4312
Jack McElroy	Battelle PNL	509-375-2532
Hartmut Witte	Waste Chem Corp.	201-588-2800

TABLE 3: ANTICIPATED VS. [EXPERIMENTAL] OFFGAS SCRUBBING EFFICIENCIES