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by

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ABSTRACT

The Large Slurry Fed Melter (LSFM) at the Department of Energy's Savannah River Plant recently completed two years of service and was shut down for evaluation. The melter operating history is reviewed and the condition of the refractories and metal components is described. The excellent condition of the LSFM verifies the expected performance of the materials of construction, and indicates that a two year melter life is achievable in the Defense Waste Processing Facility (DWPF).

BACKGROUND AND INTRODUCTION

The Savannah River Plant (SRP) has operated for over thirty years producing nuclear materials for defense, space, and medical use. The site is located near Aiken, South Carolina, occupying over 300 square miles along the Savannah River. During operation SRP has generated about 30 million gallons of high-level radioactive waste.

The waste, a product of radiochemical separation processes, is stored in large underground tanks. It consists of three discrete fractions: an insoluble sludge (primarily hydroxides of iron, aluminum, and manganese), a saltcake, and a saturated supernate solution. Approximately 65% of the total radioactivity is in the sludge, which contains insoluble long-lived radionuclides and virtually all of the actinides. The salt and supernate contain Cs-137, which accounts for most of the balance of the radioactivity.

For the past ten years, the Savannah River Laboratory (SRL) has been developing a process for immobilizing the waste by incorporating it into a borosilicate glass [1-6]. In this process, the waste sludge is first treated to remove soluble salts and excess aluminum. The redissolved saltcake and supernate solution are decontaminated by a precipitation process which removes cesium and strontium for recycle to the sludge stream. The sludge is then blended with a borosilicate glass powder and the resultant slurry is fed directly to a continuous Joule-heated ceramic melter operating at 1150°C. Effluent gasses are decontaminated by an extensive off-gas treatment system [4]. The waste glass is cast into 2 ft diameter by 10 ft tall stainless steel canisters which are decontaminated, welded shut, then temporarily stored on site pending designation of a federal repository.

The goal of SRL's waste vitrification development work has been to develop the technology for the design of the Defense Waste Processing Facility (DWPF). Early work involved laboratory and small scale melting equipment. As the program matured, larger equipment was developed and tested. Recent efforts have focused on a large scale vitrification pilot facility. Two large scale melter systems have been operated since October of 1980 and a third is scheduled for startup in mid 1985. Continuous melter campaigns have lasted as long as 63 days, demonstrating the slurry fed vitrification process for the DWPF.

SRL's second large scale melter, the Large Slurry Fed Melter (LSFM), completed a successful two year experimental program in February 1984 (Figure 1). The melter was shut down, drained of glass, and its condition was evaluated by inspection and disassembly.

LSFM OPERATION

The LSFM produced over 240 tons of glass in its lifetime, more than any other SRL melter. It has been fed slurries of simulated average SRP waste with glass frits 131, 165, and 168 [1]. The sulfate level (approximately 0.16% of the glass) was of particular interest with respect to metal corrosion. Of the LSFM's 749 days operating time, 193 days (25%) were spent feeding the melter. The rest of the time was spent idling at 1100 to 1150°C. The glass contact refractory was Monofrax K-3 (TM Carborundum Co.) and the metal components (electrodes, thermowells, level detector) were made of Inconel 690 (TM Inco Alloys International). The melter was of composite refractory construction. The glass contact refactory was chosen for durability in contact with the glass pool. Outer refractory layers were selected for thermal insulating properties.

LSFM CONDITION

Inspection and measurement began after the LSFM was shut down and drained. The melter was in excellent condition overall with very little loss of material from the refractory or the electrodes (Figure 2). Several experts in the fields of refractories and metals corrosion were invited to inspect the melter. All agreed, based on the final condition of the LSFM's Inconel 690 and Monofrax K-3 components, that the DWPF melter will have no difficulty attaining the 2-year design lifetime.

REFRACTORY PERFORMANCE

Monofrax K-3, the glass contact refractory, is composed of 60-65% solid solution crystals of chromia-alumina, 3 to 4% glass, and the remainder a complex magnesia-chromia-alumina spinel. Maximum corrosion loss from the K-3 was less than 3/4 inch and occurred at the melt line and immediately above the throat. This corresponds to a rate of approximately 1 mil/day, significantly better than that previously experienced [7,8]. The Carborundum Co. has identified the K-3 corrosion mechanism as being a strong function of the nickel oxide and iron oxide content of the glass. The magnesium and aluminum in the K-3 spinel phase were replaced by nickel and iron forming a chrome-nickel-iron spinel as a final reaction product. Micrographs clearly showed a distinct boundary between the parent K-3 and the Ni- and Fe-rich reaction layer.

There was some cracking and spalling evident above the melt line. Four of the LSFM K-3 blocks were returned to the Carborundum Co. for detailed analysis. They found that the cracking and spalling evident near the melt line is due to thermal shock and cannot be eliminated. However, the majority of the damage was restricted to the exposed corners and did not propagate far into the blocks. Spalling occurred primarily at protruding upper corners of the refractory blocks. In this location when cracking occurred the pieces were not keyed together and could fall off into the melt pool. In the current DWPF melter design, there are no horizontal joints or corners in the cold cap zone. This should minimize spalling even though thermal shock cracking is inevitable.

Glass penetration into joints between K-3 blocks was evident, as expected, throughout the melter below the melt line. In the side walls, the glass typically migrated as far as the backup Zirmul (TM Didier-Taylor Co.) blocks and stopped. There were a few locations, however, where joints in the backup blocks coincided with joints in the K-3 and glass migrated to the high-alumina castable layer. This occurred predominantly near corners and around the riser section. The glass flow was arrested at that layer by increased viscosity due to the dissolution of alumina in the glass and the thermal profile through the refractories. Glass penetration along the electrode busses halted at the same approximate depth.

The floor of the melter was in good condition with less than 1/4 inch loss of material. There was a uniform layer of glass approximately 1/2 inch thick left after draining. There was also a random, thin layer of crystalline material, varying from 1/16 inch thick on the center of the floor to 1/2 inch thick in corners and at the bottom of the throat. The crystalline material was primarily a chromium-nickel-iron spinel, confirming Carborundum's assessment of the K-3 corrosion mechanism. Glass penetration into floor joints was not as extensive as was seen in the wall joints. Where glass did migrate between the K-3 blocks, it was stopped by a layer of K-3 cement immediately below the blocks. Very little penetration was evident around the drain valve as the cooled valve probably prevented penetration by increasing glass viscosity.

INCONEL 690 PERFORMANCE

Inconel 690 (29% Cr, 9% Fe, balance Ni) is the reference glass contact alloy for DWPF melter fabrication [7]. Uses in the LSFM included plenum heater sheaths, thermocouple protection tubes, glass level detectors, off-gas piping, drain valves, pouring trough, pouring spout, and melter electrodes. Inconel 690 melts at 1350°C, so it is important to maintain melter operating temperatures not much higher than 1150°C. With adequate temperature control, Inconel 690 maintains sufficient creep resistance for massive self-supporting melter components. The high chromium content of the alloy gives it exceptional resistance to oxidation and sulfidation. In other tests, it has survived where a nickel based alloy with lower chromium content (Inconel 601) was penetrated by sulfidation/oxidation agents [8]. Inconel 690 is protected at high temperatures by a layer of $Ni(CrFe)_2O_4$ and $(CrFe)_2O_3$ that forms during the initial heating period [9]. This layer impedes further oxidation by acting as a diffusion barrier. Similarly, the barrier resists the formation of reduced sulfides that lead to the autocatalytic sulfidation reaction.

Predictable electrode life is of major importance since electrodes are irreplacable, and necessary for melter operation. The Inconel 690 electrodes were in excellent condition, which is attributable to the alloy's high chromium content, and very good temperature control during the melter's operating life. The corners of the electrodes showed general rounding, and little material loss. Corners are generally the region of maximum wear, since electrical currents and glass velocities are highest in this section of the electrode. Weld beads where the vertical electrode plates were joined to "feet" showed essentially no material loss. The bottom edges of each of the electrodes, and electrode feet showed no significant material loss. In fact, the original machining marks were visible in a number of locations. The largest decrease in electrode thickness, ignoring edge rounding, was 0.23 inch (0.3 mils per day). This occurred adjacent to the top edge of one of the footed electrodes. Approximately 80 mils (35%) of the loss was on the backside of the electrode, where a half-inch gap developed between the back of the electrode and the refractory wall. Thus, no significant material loss was seen in the electrodes, which appeared to have several more years of possible use. Inco Alloys International is measuring the effect of the sustained high temperature exposure on the strength, ductility, and impact strength of the Inconel 690.

Examination of other Inconel 690 components indicated similar behavior. The average corrosion rate of a thermowell in service for 302 days was 0.12 mils/day, the same value reported for electrodes in an earlier study [7]. Localized attack was at a maximum approximately seven inches below the melt line, and corresponds to a corrosion rate of 0.21 mils/day. This is the glass region where temperatures are typically high, and horizontal velocities resulting from convection cells are greatest [10].

The highest rate of attack of any of the Inconel 690 components occurred in the replaceable liquid level detector. This bubbler type detector functions by determining the hydrostatic head difference between a vent above the glass melt, and argon bubbled into the glass pool at a fixed location above the melter bottom. During 492 days of continuous service, with an argon flow rate of 3 scfh, the hole enlarged vertically at the average rate of 3.5 mils/day. This was the result of high local glass velocities as bubbles rose from the vent. Lateral and downward enlargement of the hole was only 0.4 mils/day.

Glass velocity effects can be compared between the LSFM and small laboratory experiments. Table 1 shows a four fold increase in the maximum rate of attack of Inconel 690 when the glass velocity is increased from stagnant conditions to 1.1 inch per second. Thus, although localized glass velocities have a measureable effect on attack rates, they do not reduce component life below the 2 year design life.

Inconel 690 is very resistant to attack in nonaqueous environments. It pits, however, in aqueous halide solutions (e.g. chloride and flouride) if there is insufficient oxidizing acid present [11]. Thus, while it is satisfactory for melter components that are maintained above the dew point of the evolved gasses, it is not satisfactory for off-gas quenchers or scrubbing equipment in low nitrate service. Such service requires molybdenum in addition to chromium in the alloy (e.g. Alloy C-276).

CONCLUSION

The generally excellent condition of the LSFM indicates that the selected materials of construction are more than adequate. Based on this experience, a two year life for the DWPF melter can be achieved, with Monofrax K-3 as the glass contact refractory, and Inconel 690 used for metallic melter components.

Thermal shock damage to the K-3 refractory is inevitable but proper design can minimize loss of material.

TABLE I

Effect of Glass Velocity on Rate of Material Loss in Defense Waste Glass at 1150°C, mils/day

Velocity	Monofrax K-2[12]		Monofrax K-3[13]		Inconel 690[13]	
(inch/sec.)	ML*	1/2H**	ML	1/2H	ML	1/2H
0	6.4	3.4	4.3	1.3	0.3	1.0
0.13	5.2	5.6				
1.1 (3 day test)			11.7	4.7	4.0	2.3
1.1 (7 day test)			6.1	3.0		

* Melt line.

** One half way between melt line and bottom of sample.

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REFERENCES

1. "Preliminary Technical Data Summary for the Defense Waste Processing Facility, Sludge Plant," DPSTD-80-38-2, Savannah River Laboratory, Aiken, SC., September, 1982.

2. R. Maher, L. F. Shafranek, and W. R. Stevens, III, "Solidification of Savannah River Plant High-Level Waste," A.I.Ch.E. Report No. CONF-83-1117, Wash. DC., November 1983.

3. F. H. Brown, et al., "Savannah River Laboratory's Operating Experience with Glass Melters." The Treatment and Handling of Radioactive Wastes, eds. A. G. Blasewitz, et al., Battelle Press, (1983)

4. John L. Kessler and Chris T. Randall, "Performance of a Large Scale Melter Off Gas System Utilizing Simulated SRP DWPF Waste," "Waste Management '84 Symp.," U. Ariz., 1984.

5. J. L. Crandall, "High Level Waste Immobilization." The Treatment and Handling of Radioactive Wastes, eds. A. G. Blasewitz et al., Battelle Press, Columbus(1983).

6. R. Maher, L. F. Shafranek, J. A. Kelley, R. W. Zeyfang, and A. J. Lethco, "The Defense Waste Processing Facility," The Treatment and Handling of Radioactive Wastes, eds. A. G. Blasewitz, et al., Battelle Press, Columbus (1983).

7. W. Nevyn Rankin, "Evaluation of Glass-Contact Materials for Waste Glass Melters," Advances in Ceramics, Vol. 8, G. G. Wicks, and W. A. Ross eds., Am. Ceram. Soc., 1984.

8. S. M. Barnes, G. J. Sevigny, and R. W. Goles, "Corrosion Experience with a Slurry-Fed Ceramic Melter," Proc. Treatment and Handling of Radioactive Wastes, ANS, April 1982.

9. P. I. Fontaine, and E. G. Richards," Hot Corrosion Problems Associated with Gas Turbines, ASTM Sp. Publ. 421, 1966.

10. D. R. Routt, "Physical Modeling of a Glass Melter Designed for Vitrification of Defense Waste," Advances in Ceramics, Vol. 8, G. G. Wicks, and W. A. Ross eds., Am. Ceram. Soc., 1984.

11. D. F. Bickford, and R. A. Corbett, "Material Selection for Defense Waste Processing Facility," Pro. Inter. Conf. Corrosion of Nickel Based Alloys, Cinc. OH, ASM, October 1984.

12. W. Nevyn Rankin, Savannah River Laboratory, Aiken SC, personal communication 1984.

13. J. F. Wosinski, "Nuclear Waste Glass Testing for Savannah River Laboratory," Corning Glass Works, Corning NY, undated.

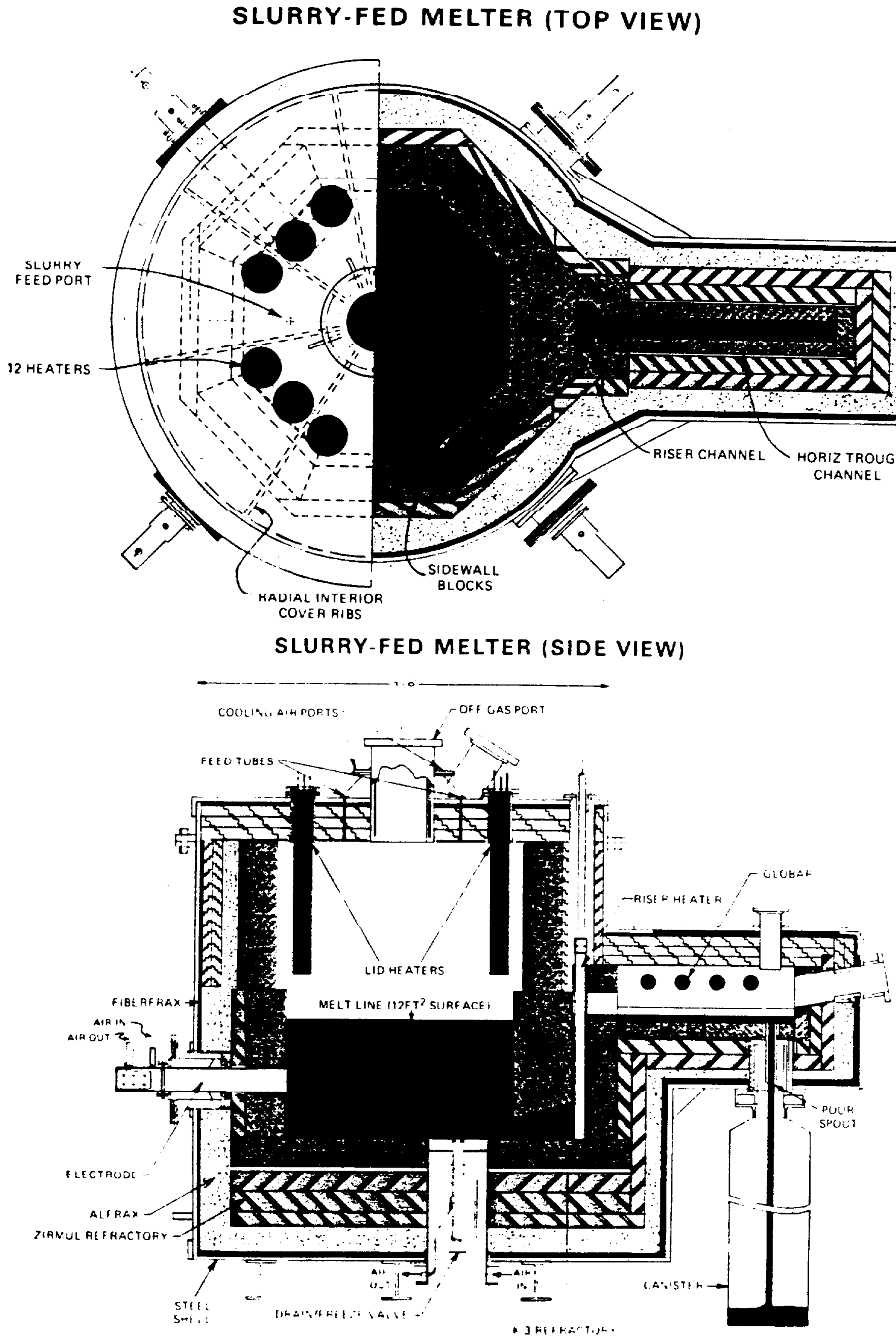

Figure 1. LSFM cross sectional views

Figure 2. View into LSFM after shutdown and draining