

MASTERA LABORATORY SCALE GLASS MELTER FOR
TESTING DEFENSE WASTE GLASS

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ABSTRACT

A one-litre joule heated glass melter was built to test the applicability of continuous melting to simulated high-level calcined defense waste. Inconel 690 electrodes and K-3 refractory brick were chosen for their corrosion resistance to fluoride glass. The melter maintained a full melt at 1100°C using 3 kW. After approximately 2 months of operation the melter was dismantled for metallurgical examination. The Inconel 690 electrodes were heavily corroded. A second melter is now in operation to verify the findings of the first melter run.

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory (INEL) reprocesses defense type nuclear fuel using a solvent extraction process.¹ The resulting high-level waste solution is calcined (dried) in a fluidized-bed process into a mixture of granules and powder known as calcine.² Zirconia calcine, which is about 50 wt% CaF₂ was the type used in the glass melting work presented in this paper. Calcine is currently stored on site,³ however, regulatory and environmental considerations may require an alternative form for disposal of high-level waste. One alternative being evaluated is a leach resistant glass containing 25-40 wt% calcine.⁴ To test the applicability of continuous

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melting to the zirconia calcine, a laboratory-scale (1 litre) joule heated melter was built to vitrify calcine at 1100°C. The materials of construction, K-3 fused cast refractory and Inconel 690 electrodes, were chosen on the basis of 10-day static corrosion tests in a molten glass environment. These tests were designed to single out the materials most resistant to fluoride corrosion since this will be the most demanding requirement on the melter. The melter was operated at 1100°C for about 2 months, after which it was dismantled for materials examination. A second modified melter is now in operation to verify findings from the first melter.

CORROSION TESTS - MATERIALS SELECTION

The major concern with melter lifetime is high temperature fluoride attack on the refractory and electrode materials as the zirconia calcine is approximately 50 wt% CaF_2 . To test prospective melter fabrication materials, 10-day corrosion dip tests were done in a glass (No. 13) containing 33 wt% simulated zirconia calcine, 34.5 wt% SiO_2 , 18.9 wt% Na_2O , 8.6 wt% B_2O_3 , 1.4 wt% Li_2O , 1.9 wt% CaO , and 1.4 wt% ZnO . Refractories were cut into samples measuring 2.5 cm x 2.5 cm x 7.6 cm and electrode materials were cut into 0.64 cm x 2.5 cm x 7.6 cm samples. These samples were then immersed about halfway in the glass to provide corrosion information on the sample in the glass phase, in the gaseous phase above the glass, and at the phase interface. The melt temperature was maintained at about 1100°C. Twice each day, 20 grams of powdered batch materials were added to each sample to maintain a realistic environment both in the molten glass and in the gaseous phase in the furnace.

Candidate electrode material compositions and 10-day corrosion data are

shown in Tables I and II. As can be seen from the data, Inconel 601 and 690 were the most corrosion resistant materials with weight losses lower than 5 wt%. Metallurgical examination of these two alloys showed that even though Inconel 601 experienced less weight loss and corrosive penetration than the 690, it is less desirable as an electrode material due to severe grain growth. Both the 601 and 690 showed similar attack in the gas phase, but in the glass phase the 601 showed substantially more grain growth. The major corrosion mode on both alloys was intergranular attack with varying amounts of internal precipitation.

Of the seven refractories tested, two (both high chrome types) showed no significant weight losses, rather a slight weight gain due to a thin glass coating. As can be seen in Tables III and IV, the five AZS (alumina-zirconia-silica) types (S-3, S-4, S-5, A, M) all high in Al_2O_3 and/or SiO_2 , showed about 3 to 5 wt% loss. The two high chrome types (K-3, E) both appear satisfactory, so on the basis of lower cost and higher electrical resistivity (to minimize current flow through the refractory) the K-3 was chosen over the E refractory.

MELTER FABRICATION AND OPERATION

The melter ceramics were bonded with a high chrome (17.59% Cr_2O_3) grout. The ceramic unit (0.2 m x 0.3 m x 0.46 m) was nested in silica insulation 10-cm thick contained in a 304L stainless steel box. Overall dimensions, feed system, tilting jack, and materials of construction are shown in Figure 1. For startup, the feed chamber was filled with bits of glass and heated with a 600-watt resistance element until the glass became conductive enough for the electrodes, half submerged in the glass, to pass current ($\sim 6000C$). Once the melt could be maintained with joule heating

TABLE I
ELECTRODE MATERIALS COMPOSITION IN WEIGHT %

Element	Inconels				Hastelloy C-4	Nitronic 50
	601	617	625	690		
Ni	60.3	54	61	60	58.3-65.3	11.5-13.5
Cr	23	22	21.5	30	14-18	10.5-23.5
Fe	14.1		2.5	9.5	3	52.4-61.3
Mo		9	9		14.0-17.0	1.5-3.0
Ta			3.65			
Al	1.35	1			1.0	4-6
Mn					2.0	0.1-0.3
Co		12.5				0.1-0.3
V						1.0
Si				0.03		
C					0.70	
Ti						

TABLE II
ELECTRODE CORROSION RESULTS

Material	wt% Loss	Penetration (mm)	
		Vapor Phase	Glass Phase
Inconel 601*	4.0	0.48	0.40
Inconel 617	18		
Inconel 625	54		
Inconel 690	4.3	0.70	0.45
Nitronic 50	34		
Hastelloy C-4	destroyed		

* Showed extensive crystal growth.

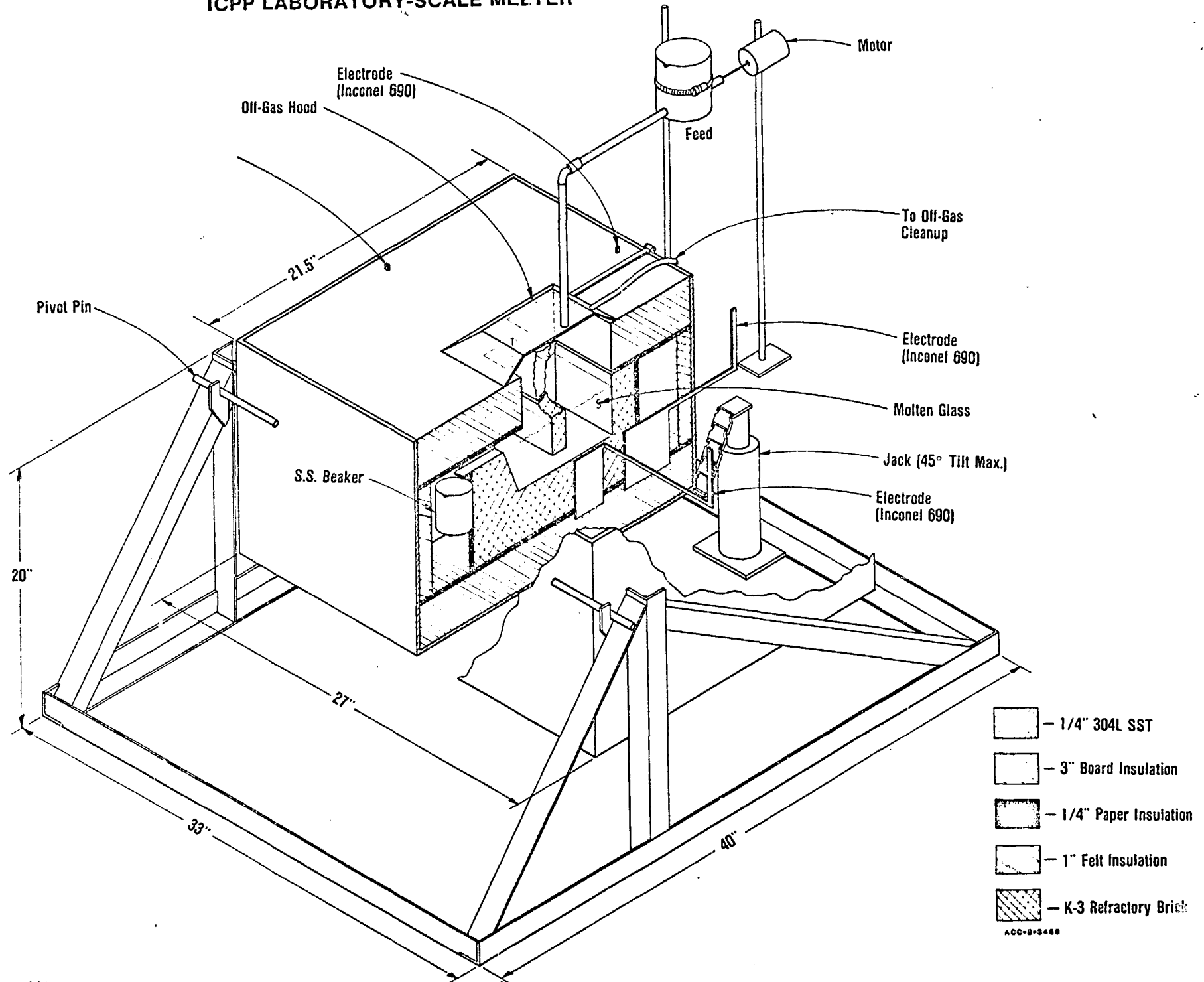
TABLE III
REFRACTORY COMPOSITIONS IN WEIGHT %

Compound	Refractory Type, wt%						
	A	K-3	E	M	S-3	S-4	S-5
Al ₂ O ₃	98.70	60.40	4.7	94.5	50.13	49.69	47.32
Cr ₂ O ₃		27.36	79.7				
Fe ₂ O ₃	0.09	4.21	6.1	0.08	0.12	0.10	0.11
MgO		6.05	8.1	0.15			
Na ₂ O	0.03	0.31		3.90	1.10	1.10	0.84
ZrO ₂					34.20	36.56	40.97
SiO ₂	0.50	1.77	1.3	1.09	14.25	12.30	10.61
CaO				0.26			
B ₂ O ₃	0.50				0.15	0.15	0.15
TiO ₂				0.02	0.05	0.10	
Other	0.18		0.1				

TABLE IV
REFRACTORY CORROSION RESULTS

Refractory, wt% lost						
K-3	E	S-5	S-3	S-4	A	M
0.0	0.0	3.4	3.7	4.5	4.9	5.1

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alone, the resistance element was moved to the pour spout to keep the pour molten. A 316 stainless steel hood was then placed over the feed cavity to reduce heat losses and to contain off-gases to be collected for analysis.

The batch feed was augered through a downspout and fell directly into the melt. As the glass level rose, hydraulic pressure through the tunnel to the fining chamber raised the level there as well. The glass could be poured by tilting the melter with a hydraulic jack and allowing the melt to overflow through an Inconel 690 pour spout and into a 400 mL stainless steel beaker. Batch materials were added to the melt in large quantities (as much as 500 gram charges) with no foaming difficulties or loss of electrical conduction. At 1100°C, the feed chamber used about 1.5 to 2.5 kW, while the fining chamber used about 0.8 to 1.2 kW. Samples of the glass poured by the melter were low viscosity, homogenous, and opaque. The 400 mL cylindrical blocks were cut into pieces which showed very little porosity or color striation whether poured over a period of several hours or as little as 10 minutes.

RESULTS

After two months of operation the melter was shutdown due to the deterioration of one of the feed chamber electrodes. The left electrode in the feed chamber had overheated and melted into the glass melt. It was found later as a solidified mass at the bottom of the chamber. The right side electrodes from both the feed and fining chambers were examined⁵ and metallographic sections were taken above and below the glass level. The corrosive attack on the electrodes was much more severe than that indicated by the 10-day tests. Both electrodes suffered precipitation through out their cross sections. This could have been caused by complete corrosive

penetration, overheating over a period long enough to precipitate carbides present in the alloy, or high current densities caused during glass pouring. The attack also included spalling of corrosion product layers and much grain growth.

The increase in corrosion rate over the 10-day tests may have been caused by temperature fluctuation during the melter run causing spalling as the AC electrical current passed through the electrodes, overheating, or perhaps the 6-fold increase in exposure time. The overheating may have been caused by a short from one of the feed chamber 220 V electrodes to either the ground electrode in the fining chamber 115 V circuit or through a molten glass path to the containing box. Some of the grout was eaten away by the glass allowing some leakage of the melt out of the chamber. The literature, our experiments, and data from outside sources indicate that there is probably no better metallic material than Inconel 690 available for use as an electrode. The use of graphite or molybdenum is not desirable, since both materials would serve only as consumable electrodes which could be difficult to use in a remote process.

LABORATORY-SCALE MELTER II

A second laboratory-scale melter is now in operation to verify whether the findings in the first melter were technical difficulties in using this melting method for high-fluoride calcine or just operating errors. The second melter uses only one electrode circuit. The fining and feed chamber electrodes are connected electrically in parallel. This change eliminates the possibility of shorting to a ground electrode in the conductive glass melt. Also, the refractory pieces were cut more carefully to reduce the joint thickness between them and thereby lessen the

possibility of glass leakage out of the chambers. During operation, the current density on the electrodes will be maintained below 0.6 A/cm^2 since above this level rapid deterioration of the electrodes has been observed.

The second melter is started in exactly the same way as the first melter. Glass No. 51 containing 21 wt% simulated zirconia calcine, 52 wt% SiO_2 , 19 wt% Na_2O , 6.3 wt% B_2O_3 , and 1.7 wt% CuO was used as the initial melter charge. The experimental plan calls for melting glass containing 21 wt% calcine for three weeks and then momentarily shutting down to replace one of the feed chamber electrodes. The used electrode can then be examined for corrosion. The following three week period will be run with glass containing 27 wt% calcine, and the last three week period with glass containing 33 wt% calcine. With an estimate of corrosion rate from each run, information will be gained on the rate of deterioration versus calcine loading in the glass. This data will provide an idea of what to expect using a continuous joule-heated glass melter to melt zirconia type calcine.

CONCLUSION

The first laboratory-scale melter was built based on short term corrosion tests, the literature, and private communications. After two months of operation, examination of the refractories and electrode materials indicated that while the K-3 ceramics faired very well, the Inconel 690 electrodes were severely corroded. To verify these findings, a new melter of similar design with slight variations to correct problems noted with the first melter was built. Tests are now being run to gain insight on how the deterioration rate of the electrodes is affected by calcine content and

therefore fluoride concentration in the glass at 1100°C.

ACKNOWLEDGEMENT

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