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OPERATION OF A LABORATORY-SCALE GLASS MELTER TO VITRIFY ICPP ZIRCONIA CALCINE

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Idaho Falls, Idaho 83401

EXXON NUCLEAR IDAHO COMPANY, Inc.

Prepared For The
DEPARTMENT OF ENERGY

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ABSTRACT

A 1.5 litre joule-heated glass melter was built to test the applicability of electric melting to vitrify simulated high-level calcined defense waste. The Inconel 690 electrodes have a high but acceptable corrosion rate and showed some phase separation. The K-3 refractory showed excellent resistance to the glass. Off-gas tests indicate negligible fluoride volatility. The melter operates at 1100°C using 1.5 KW. The melter has been dismantled for metallurgical examination and modified twice. The third version is now in operation.

SUMMARY

A 1.5 litre joule-heated glass melter was built to test the applicability of electric melting to the vitrification of ICPP calcined wastes. 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 using borosilicate frits and zirconia calcine. The melter was started up several times using auxilliary resistance heating until the glass was conductive enough for joule heating to maintain the melt. The auger feed system delivered 15-30 g/min of powdered feed to the melter. Melting temperature was measured with a thermocouple and an infrared pyrometer. The particulate and fluoride content of the melter off-gas was small. The melter poured about 30 kg of glass samples that were low viscosity, homogeneous, and comparable in leach resistance to samples made in crucibles in the laboratory. Electrodes were periodically changed out for metallurgical examination. The K-3 refractory showed excellent corrosion resistance to the glass whereas the Inconel 690 electrodes had a high but acceptable corrosion rate.

Results indicate the possibility of Cr/Ni phase separation at high temperature in the Inconel 690 electrodes and the need for tight control of temperature to prevent preferential heating of high temperature-low resistance areas.

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I. INTRODUCTION

At the Idaho Chemical Processing Plant (ICPP) high-level radioactive waste is calcined into a mixture of granules and powder known as calcine.[1] One option being considered for permanent storage of this waste is to vitrify a mixture of calcine and glass formers into a leach-resistant, non-dispersible glass.[2] Zirconia calcine, which is about 50 wt% CaF_2, is the type of waste used in the glass melting work presented in this paper. To test the applicability of continuous melting to the zirconia calcine, a laboratory-scale (1.5 litre) joule-heated melter was built to vitrify calcine at 1100°C. This report summarizes fabrication, and 30 months of testing and operation of the original melter including two modifications of the original design. Feeding, off-gas and corrosion data were obtained.

II. CORROSION TESTS FOR MATERIALS SELECTION

The major concern with melter lifetime is potential high temperature fluoride attack on the refractory and electrode materials due to the CaF_2 (approximately 50 wt%) in the zirconia calcine (see Table I). 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.[3] Refractories were cut into samples measuring 2.5 x 2.5 x 7.6 cm and electrode materials were cut into 0.64 x 2.5 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.

TABLE I

COMPOSITION OF ICPP SIMULATED ZIRCONIA CALCINE

Compound	Wt%
Al_2O_3	13-17
ZrO_2	21-27
CaF_2	50-56
CaO	2-4
NO_3	0.5-2
B_2O_3	3-4
Misc.	0.5-1.5

Candidate electrode material compositions and 10-day corrosion data are shown in Tables II and III. 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 examinations of these two alloys showed that even though Inconel 601 experienced less weight loss and less corrosive penetration than the 690, it is less desirable as an electrode material because of 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 (see Figures 1 and 2). Therefore 690 was chosen over 601. The major corrosion mode on both alloys was intergranular attack with varying amounts of internal precipitation.

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*Inconel is a registered trademark of Huntington Alloys Inc.

TABLE II

ELECTRODE MATERIALS COMPOSITION IN WEIGHT %

	Inconels					
Element	601	617	625	690	Hastelloy C-4	Nitronic 50
Ni	60.3	54	61	60	58.3-65.3	11.5-13.5
Cr	23	22	21.5	30	14-18	20.5-23.5
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	

TABLE III

ELECTRODE CORROSION RESULTS

		Penetration (mm)	
Material	Wt% lost in 10 days	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		

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* Showed extensive crystal growth.

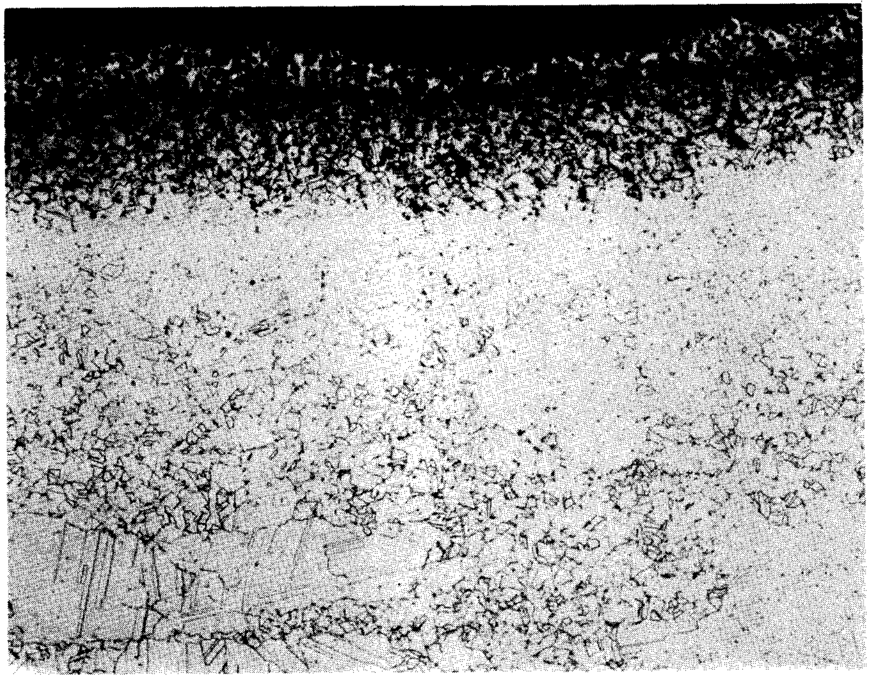

Figure 1. Photomicrograph of Inconel 690 Corrosion Test Coupon After 10 Days in Glass 13 at 1100^{o}C

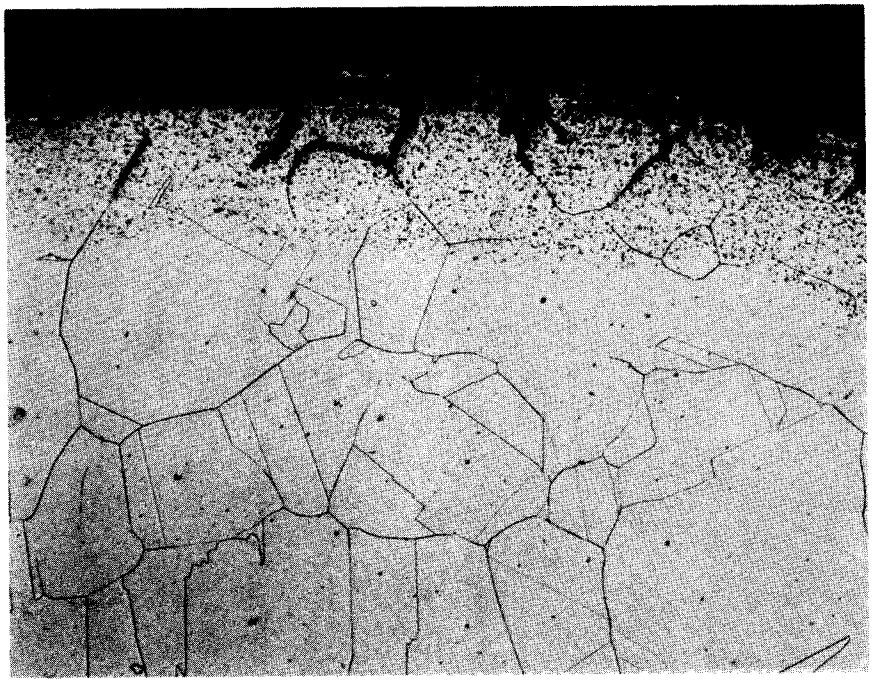

Figure 2. Photomicrograph of Inconel 601 Corrosion Test Coupon After 10 Days in Glass 13 at 1100^{o}C

Of the seven refractories tested, two high chrome refractories, Monofrax* K-3 and E, showed no significant weight losses during the 10 day tests; instead a slight weight gain due to a thin glass coating was noted. 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 a 3 to 5 wt% loss (see Tables IV and V). The K-3 and E both appear satisfactory, so on the basis of lower cost and higher resistivity (to minimize current flow through the refractory), the K-3 was chosen over the E refractory.

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*Monofrax is a registered trademark of the Carborundum Co.

TABLE IV

REFRACTORY COMPOSITIONS

	Refractory Type, wt%						
Compound	A	K-3	E	M	S-3	S-4	S-5
Al_2O_3	98.70	60.40	4.7	94.5	50.13	49.69	47.32
Cr_2O_3		27.36	79.7				
Fe_2O_3	0.09	4.21	6.1	0.08	0.12	0.10	0.11
MgO		6.05	8.1	0.15			
Na_2O	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_2O_3	0.50				0.15	0.15	0.15
TiO_2				0.02	0.05	0.10	
Other	0.18		0.1				

TABLE V

REFRACTORY CORROSION RESULTS

Refractory, wt% lost in 10 days						
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

III. MELTER FABRICATION

The melter ceramics were bonded with a high chrome (18% Cr_2O_3) grout. The K-3 ceramic refractory (0.2 x 0.3 x 0.46 m) was nested in 10cm thick Fiberfrax* alumina-silica insulation contained in a 304 stainless steel box. Overall dimensions, feed system, tilting jack, and materials of construction are shown in Figure 3. The two melting chambers are each 6" wide and 4" deep. The rear chamber measures 3" front to back and the front chamber is 2". The front walls of both chambers are sloped toward the middle to facilitate pouring. Electrode arms rest on top of the ceramics and two of the electrodes are equipped with quick disconnects to allow electrode replacement for examination without shutting down the melter.

The original melter design used a 220V source to heat the feed chamber (rear) and a 110V source to heat the fining chamber (front). Both chambers were equipped with voltage and current meters and were controlled with current limiting or temperature set point devices. The schematic for this system is shown in Figure 4. The heating system was intended to allow individual control of the two melting chambers.

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* Fiberfrax is a registered trademark of the Carborundum Co.

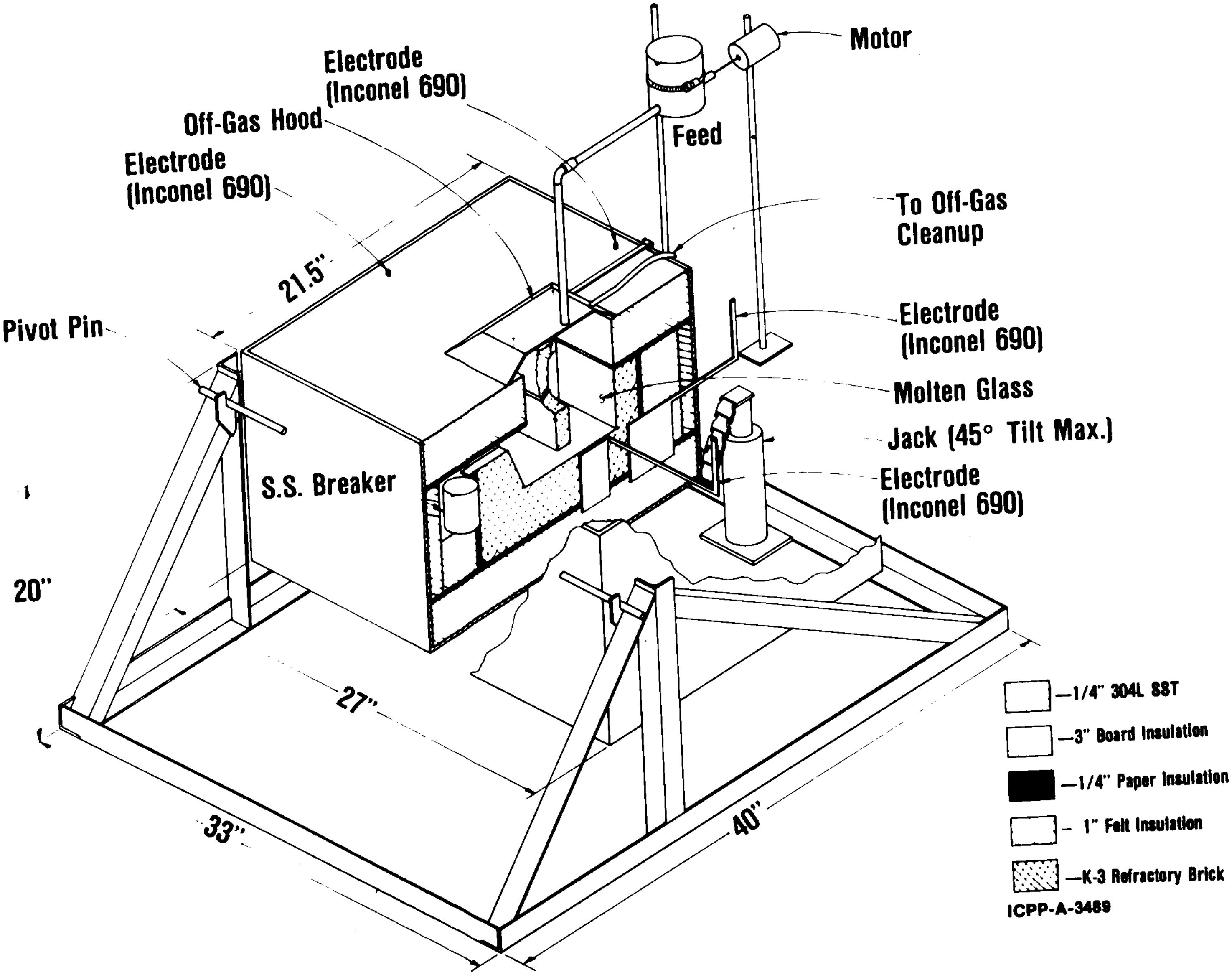

Figure 3. Cutaway View of Laboratory-Scale Glass Melter

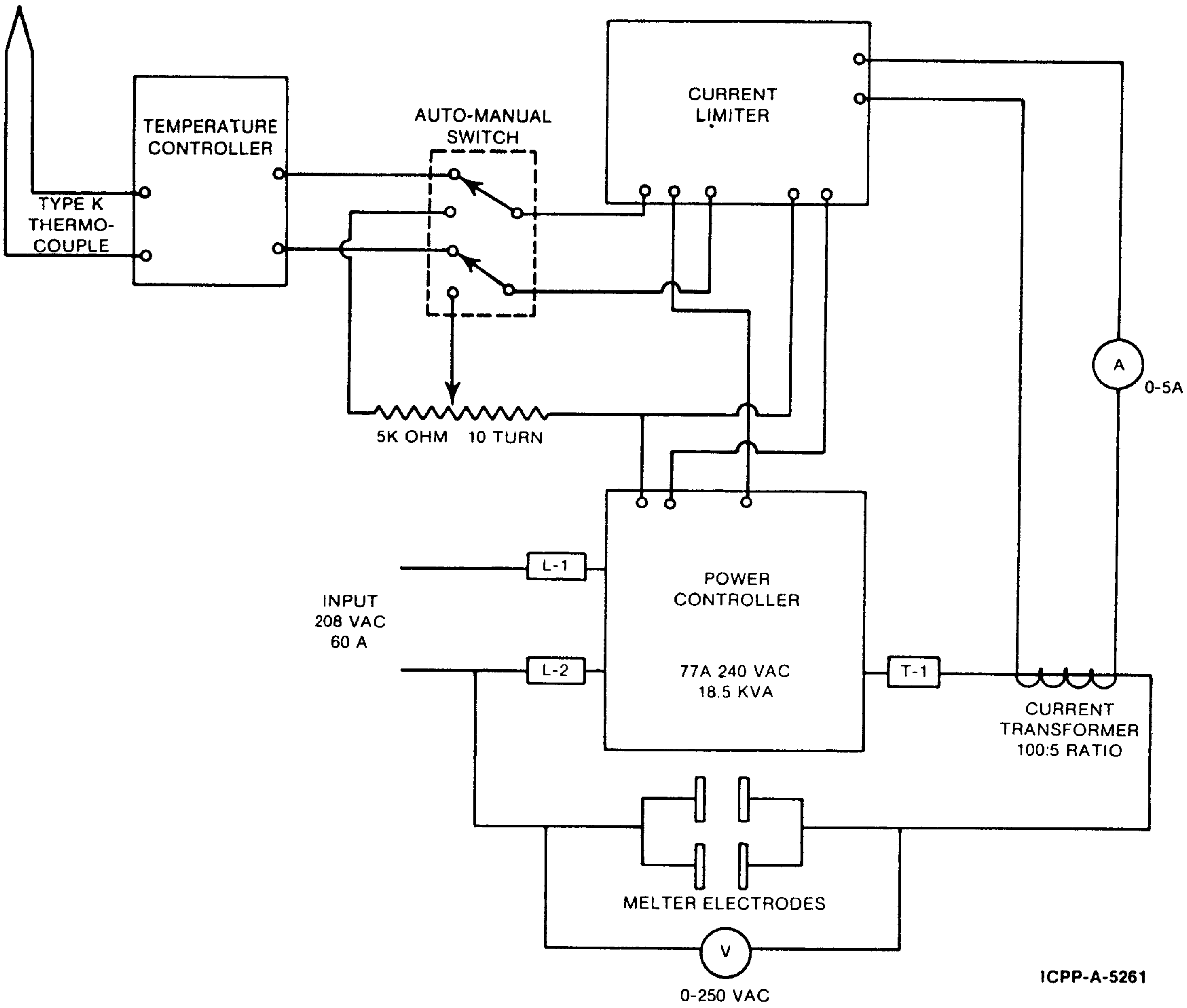

Figure 4. Control System for Laboratory-Scale Melter Power

IV. MELTER OPERATION

A. Melter Startup

For startup, the melt chambers were 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 (600°C). Once the melt could be maintained with joule-heating 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. This start-up procedure was successfully used more than 8 times with the melter in a completely cold initial condition. Care was taken to maintain no more than a $4A/in^2$ current density on the electrodes to reduce the electrode corrosion rate.

B. Melter Feed System

The melter was fed either a frit-calcine or a batch chemical calcine mixture. The first melter was started up and fed with frit 13. The modified versions of the melter operated with frit 51 and later frit 127. Frit compositions[3] are shown in Table VI. The feed was augered from a stainless steel beaker through a water cooled pipe in the melter hood. The beaker was pneumatically vibrated to prevent bridging of the feed. The feed pipe was not cooled originally, but sintering of the feed in the end of the pipe exposed to the radiant heat from the molten glass necessitated cooling. The auger delivered feed at 15-30 g/min. Feed was also introduced by hand with a scoop.

TABLE VI

FRIT COMPOSITIONS FED TO THE MELTER

	Frit Composition (wt%)		
Oxide	13	51	127
SiO_2	51.8	66	70.4
B_2O_3	12.9	8	8.5
Na_2O	28.2	24	12.8
Li_2O	2.1	——	6.2
CuO	——	2	2.1
CaO	2.9	——	——
ZnO	2.1	——	——

C. Melter Temperature Measurement

The melter temperature was measured three ways. The most accurate method was to insert a thermocouple into the glass while the electrode power was off. To avoid an inaccurate reading due to cooling of the glass by the thermocouple, the electrode power was turned back on with the thermocouple in the glass. After several minutes, the power would be turned off and the temperature read by connecting the thermocouple to an indicator. This method presented possible thermowell or sheath corrosion problems and an electrical shock hazard to operators.

A second method which measured glass temperature indirectly was tested. Thermocouples were suspended above the melt surface and their readings were calibrated to the actual glass temperature as measured by the above method. A temperature controller utilized this reading to regulate electrode current. The relationship between temperature above and below the melt surface was highly dependent on cold cap thickness and melt level. This caused unreliable feedback to the controller, so reliable temperature measurement and set-point control of the melter by this method was not achieved.

The glass temperature was also measured with an infrared pyrometer. Reading the temperature of the surface to obtain the melt temperature is subject to glass thickness and condition of the surface. To get consistent readings, the power is turned off, and the cold cap is broken. The pyrometer then read the radiation directly from the molten surface. This method was safe and easily reproduced, but supplies only an instantaneous measurement and requires a temporary power outage.

D. Melter Off-Gas System

For the off-gas experiments, the glass melting effluents were drawn from the melter hood, through a glass fiber filter, two 500ml caustic bubblers and through a rotameter to a vacuum line (see Figure 5). Off-gas was sampled at a flowrate of 1.0-2.5 l/min. The fiber filter was weighed before and after each experiment and weight gain was interpreted as particulate carryover in the off-gas. The caustic (0.5 $\underline{M}$ NaOH) bubblers were analyzed for fluoride, which is potentially volatile, corrosive, and influential on glass melt viscosity.

E. Glass Pouring

About 1080g of glass drained from the melter fills a 400 ml stainless steel beaker in one pour. The pouring space and refractory pour spout are heated with a 600 W resistance element placed immediately above the spout and is controlled with a Variac variable transformer. The pour spout is heated for 2-3 hours before pouring to ensure low viscosity glass flow to the beaker. After heating, the beaker and pour spout are at approximately 800-900°C. At this time the hydraulic jack is actuated to elevate the rear of the melter causing a maximum tilt of 45°. The glass flows from the rear chamber through the under-flow tunnel into the front chamber, and from there through the pour spout into the stainless steel beaker. The level of the glass in the beaker is viewed through an opening in the front of the melter box. After 7-15 minutes, depending on melt temperature (1000-1100°C) and degree of melter tilt (20-45° for pouring), the melter tilt angle is decreased to horizontal as the beaker fills.

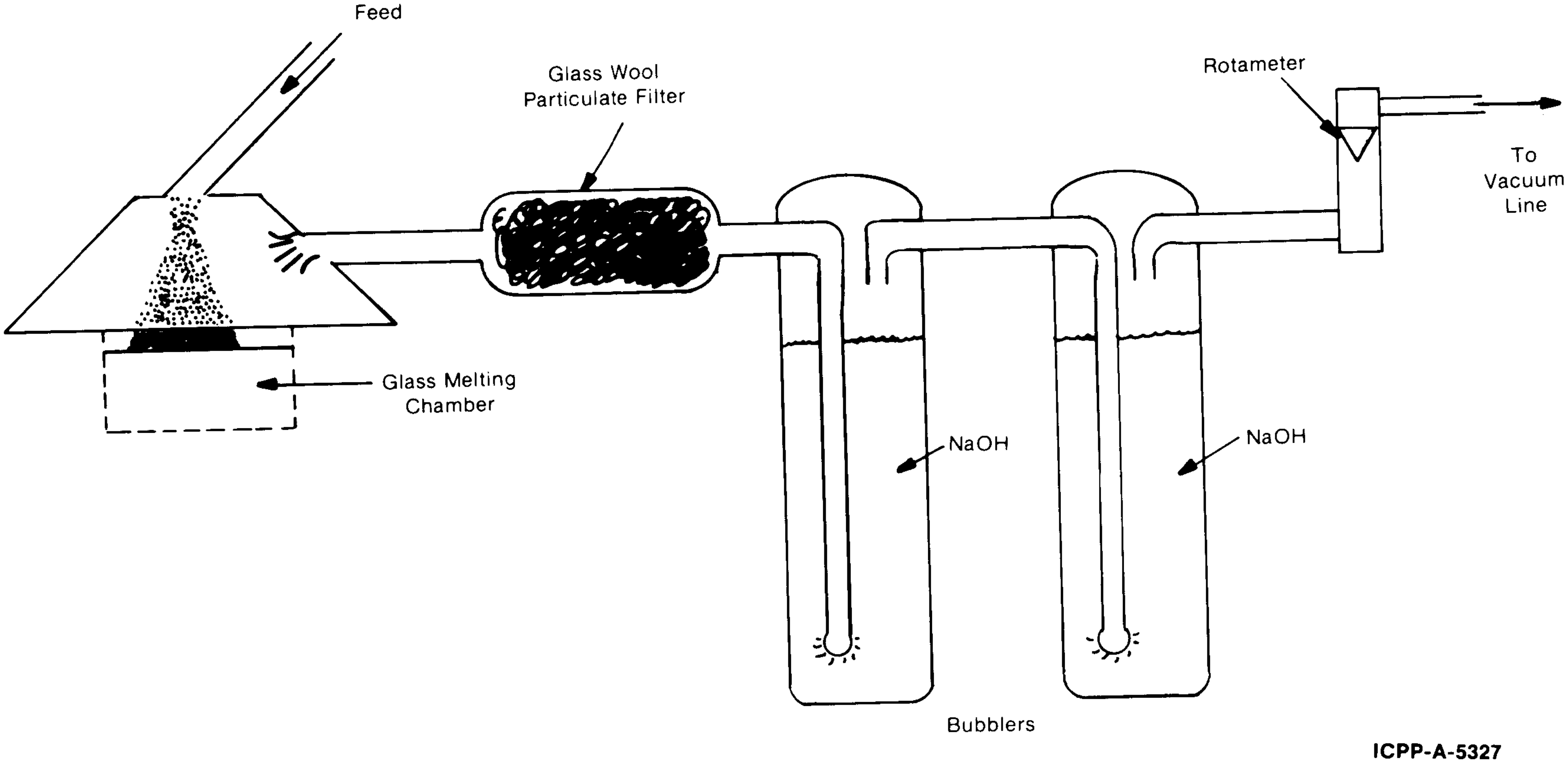

Figure 5. Off-Gas Collection System for the Laboratory-Scale Glass Melter

If the filled beaker is left in the pouring chamber, it cools slowly due to the heat conducted from the melter refractory. This yields a very smooth surface on the solidified glass with a slight (1/4 - 1/2") indentation left due to contraction on cooling. The slow cooling allows the block to cool and solidify uniformly, thus resulting in a uniform contraction. Contrarily, if the beaker was immediately removed from the melter and cooled rapidly in air, a 1-2" deep shrinkage void formed in the center at the surface of the glass. During rapid cooling, the glass near the beaker walls solidifies first, then the center and bottom of the glass cool more slowly and contract forming the void.

F. Electrode Changeout

Electrodes can be removed from the melter by turning the power off, removing the covering insulation, disconnecting the electrode from the power cable, and lifting the electrode out of the molten glass. The new electrode is installed by reversing the process. The electrodes are removed for sectioning and metallurgical examination at the end of scheduled tests and when they occasionally fail.

V. RESULTS AND DISCUSSION

A. Glass Production

The glass produced by the melter is homogeneous, low viscosity and has comparable crystallinity, density and leachability to the small glass melts done in crucibles in the laboratory.[4] The batch or frit materials mixed with the calcine melted readily in the melter with no foaming and no unmelted inclusions in the poured glasses. These glasses were obtained when material was rapidly fed to the melter in 500-600 g increments (about 15% of the melter capacity) in less than 15 minutes.

B. Testing of Auxilliary Systems

The tilting mechanism of the melter worked reliably. The feed system had two problems that were remedied. The first, previously mentioned, was the need to water cool the feed line to prevent the feed from sintering in the line. The other difficulty was that the original auger broke due to flexing fatigue, but this was corrected by substituting a spring-steel auger. Melter startup with the resistance element to heat the glass to the point at which joule heating can maintain the melt is simple and easily accomplished, though the auxilliary heating elements do need to be replaced as they periodically burn out.

The melter off-gas system worked without problem. Preliminary results show insignificant dusting or fluoride volatility. Analysis of the caustic bubbler solutions indicate that fluoride volatility was less than 0.02 wt% of the total fluoride (80 g) contained in the kilogram of feed augered to the melter during each test. This low volatility was measured regardless of whether the test continued until the cold cap was sintered down to a thin crust on the melt 25 hours after feeding ended, or if the test terminated 4 hours after feeding when a loose 2 cm thick cold cap still covered the melt. The weight gain of the filter gathering the particulates carried over during the test was less than 0.5 wt% of the feed. Further investigation using a non-glass capture system to reduce the loss of Cs and F between the melt and the bubblers should be done. These tests would be easier to implement on a pilot scale melter where the loss of trace amounts of volatiles would not be as important.

Independent experiments done by L. D. Pye of New York State College of Ceramics, Alfred University indicate that N_2, O_2, NO and CO_2 are evolved from the glass melt. This study also shows that trace amounts of B, Cs, F and Sr volatilized, but react with Si and O_2 in the system and deposit on any relatively cool surface.

C. Melter Modifications

The original melter was difficult to control because of the method used to power electrodes. The electrodes in the front chamber were connected to a 110V power source while the rear electrodes were powered by a 220V source. Because the current limiter for the rear electrodes limited only one leg of the circuit, the other leg could fire uncontrolled through the conductive glass to the ground of the 110V circuit in the front chamber. This shorting of the 220V circuit to the ground of the 110V electrode circuit caused severe overheating that melted the right front eletrode after two months of service. This problem was remedied by eliminating the 110V circuit and putting both pairs of electrodes in parallel on the 220V circuit. This modification though, can also result in uneven heating between the two chambers. Because both chambers are in a parallel circuit, current will preferentially flow through the chamber having the lower resistance. This overheating caused the loss of an electrode after 8 months.

Within limits, the resistance of the chambers can be matched by adjusting the space between each pair of electrodes. To adjust the electrode spacing to match the resistances is difficult and impractical because it can only be done by turning off the power and manually manipulating parts covered with molten glass at 1100°C. A controllable but superficial parameter for keeping the glass chambers evenly heated is to adjust the amount of insulation on each chamber to balance heat losses. The second melter modification included adding insulation to the front chamber. This melter is still in operation after 7 months. During the next melter shutdown, the electrode power system will be modified such that each pair of electrodes will have separate control systems. The two systems will independently control each of the two melting chambers. This will allow separate heating of each chamber yielding even heating and possibly longer electrode life.

Experience to date indicates that a melter with a two electrode system, or no more than one conductive path possible per circuit, is desirable.

D. Corrosion Results

The data from the 10 day scoping studies to measure the corrosion rate of electrode and refractory materials in ICPP wastes has been supplemented by analyzing the parts actually used in the melter. Refractory materials were examined after the melter internals were disassembled. The only apparent change in the refractories was some cracking probably due to temperature cycling during the testing of melter startup capabilities. Very little glass had leaked beyond the refractories and none had passed the first layer of insulation.

The electrodes from the first melter were severely attacked due to the extreme temperature excursion described previously that melted one electrode, but these results are not typical of normal operation. The electrodes from the first melter modification yielded more useful data. These electrodes had probably spalled off more corrosion products than is normal in a production-scale melter because of the more frequent and drastic temperature cycling during testing.

Electrode corrosion tests were run with the first melter modification. These tests were done by running the melter with glass containing 21, 27, and 33 wt% zirconia calcine, each for three weeks, pouring one 400 ml beaker of glass each week. At the end of each period the left rear electrode was replaced and examined. An electrode operating in the melter during all three tests was removed after 18 weeks and examined for an overall measurement. As shown in Table VII and Figures 6 through 11, the rate of penetration of the Inconel 690 electrode material increases with increasing calcine content. The three week measurements also indicate that the glass causes corrosive penetration to occur at least twice as rapidly as the off-gases during the test period. This is contrary to the results from the scoping studies which indicated that the glass off-gases are more corrosive than the glass itself. This is probably due to the fact that the electrode area above the glass level in the melter is cooled by the surrounding air, whereas in the scoping studies, the entire electrode sample was at the same temperature.

TABLE VII

INCONEL 690 ELECTRODE CORROSION RATES FROM
THREE WEEK MELTER TESTS

Calcine Content In Glass 51 (wt%)	Corrosive Penetration Rate (mm/mo) Glass Phase	Gas Phase
21	0.73	0.22
27	0.84	0.13
33	1.63	0.22
Overall (18 weeks)	0.88	0.06

The corrosion penetration measurement of the 18 week sample indicates that after the initial attack a layer is probably formed that slows further corrosion. However, this protective layer is easily destroyed by spalling caused by thermal cycling or shock. Microscopic examination indicated a potential problem of phase separation in the electrodes (see Figures 12 and 13). Elemental analysis shows a chrome-rich phase (area 1 of Figure 13) forming at the nickel-rich grain boundaries (area 2 of Figure 13). This Cr-rich phase is apparently more brittle than the base metal and therefore more susceptible to cracking due to thermal shock. This cracking can spall off the corrosion products exposing more of the base metal to direct attack.

By the use of massive (thick) electrodes, the electrodes in a full-scale melter should be operable for at least two years.

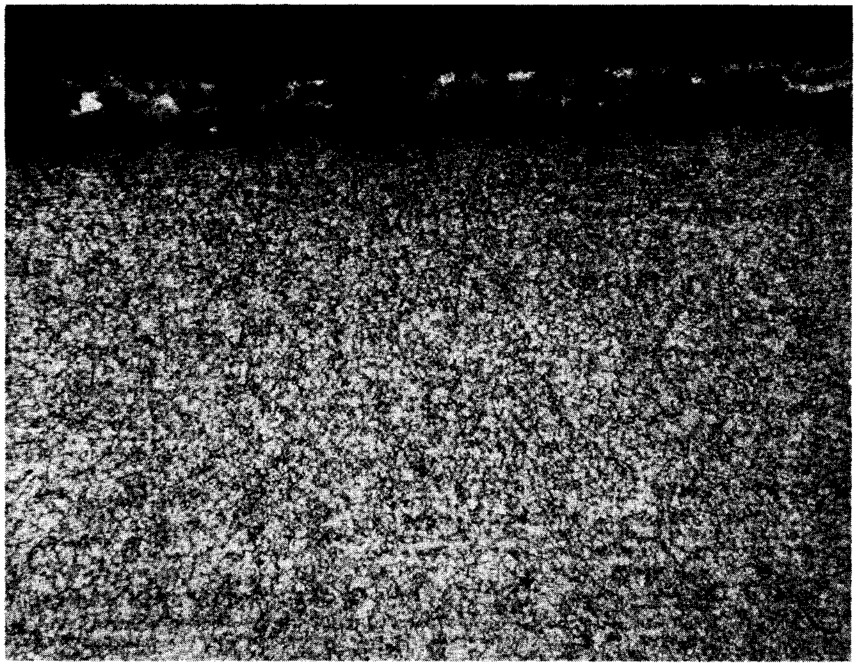

Figure 6. Photomicrograph of Inconel 690 Electrode Exposed to Gas Phase from Glass Containing 21 Wt% ZrO_2 Calcine

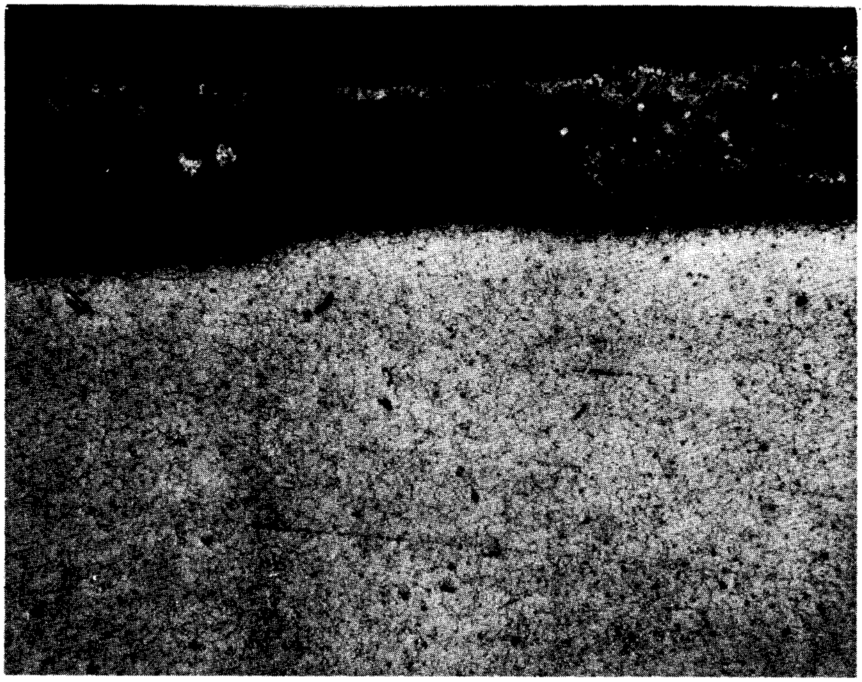

Figure 7. Photomicrograph of Inconel 690 Electrode Exposed to Glass Containing 21 Wt% ZrO_2 Calcine

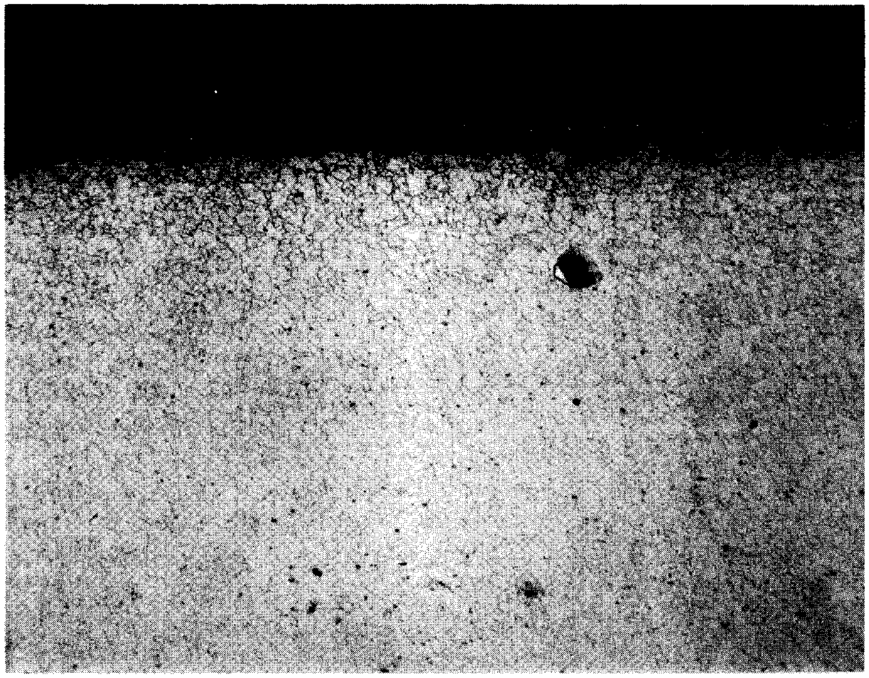

Figure 8. Photomicrograph of Inconel 690 Electrode Exposed to Gas Phase from Glass Containing 27 Wt% ZrO_2 Calcine

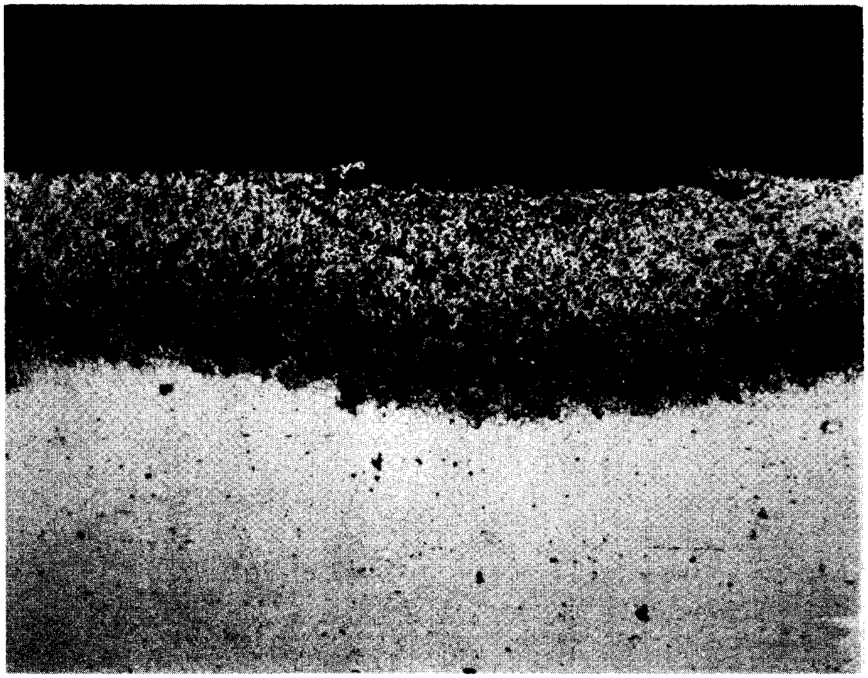

Figure 9. Photomicrograph of Inconel 690 Electrode Exposed to Glass Containing 27 Wt% ZrO_2 Calcine

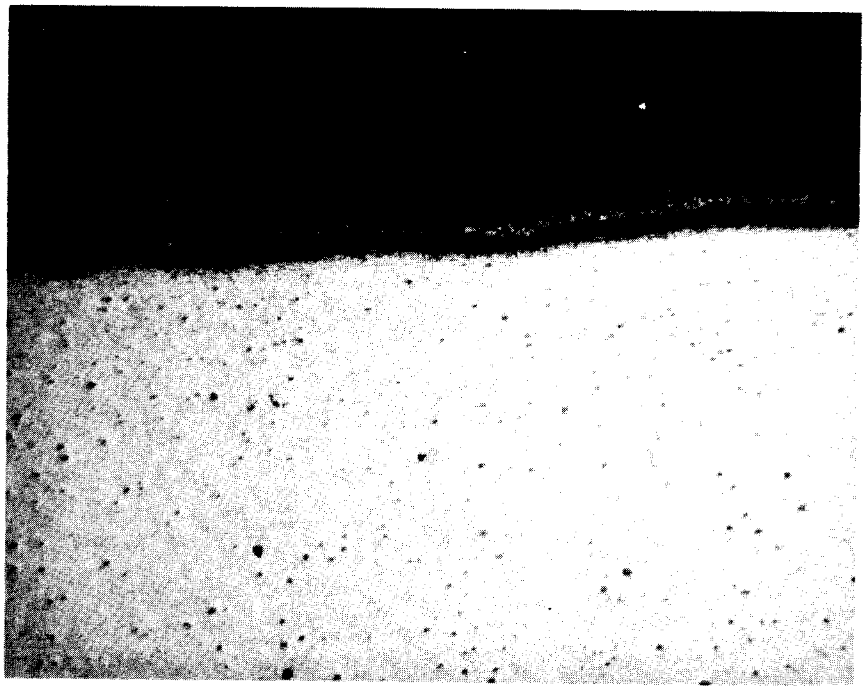

Figure 10. Photomicrograph of Inconel 690 Electrode Exposed t
Gas Phase from Glass Containing 33 Wt% ZrO_2 Calcin

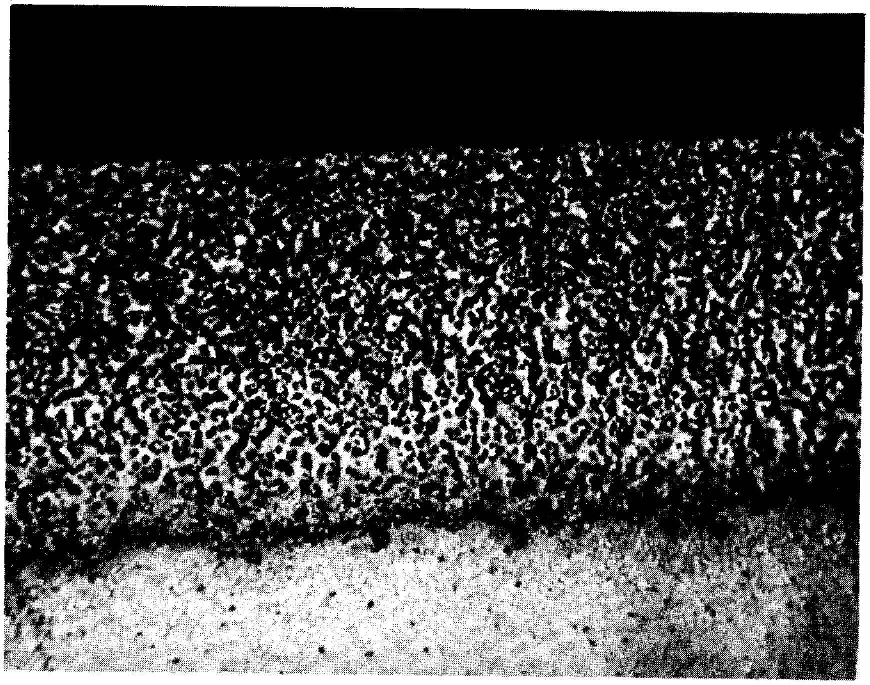

Figure 11. Photomicrograph of Inconel 690 Electrode Exposed to Glass Containing 33 Wt% ZrO_2 Calcine

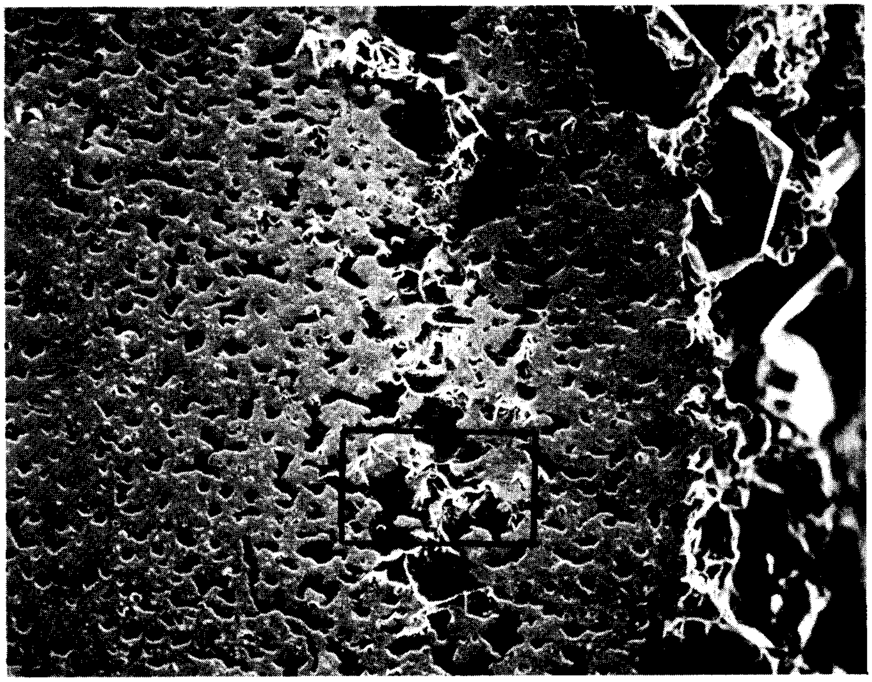

Figure 12. SEM Photomicrograph of Inconel 690 Electrode Showing Ni/Cr Phase Separation

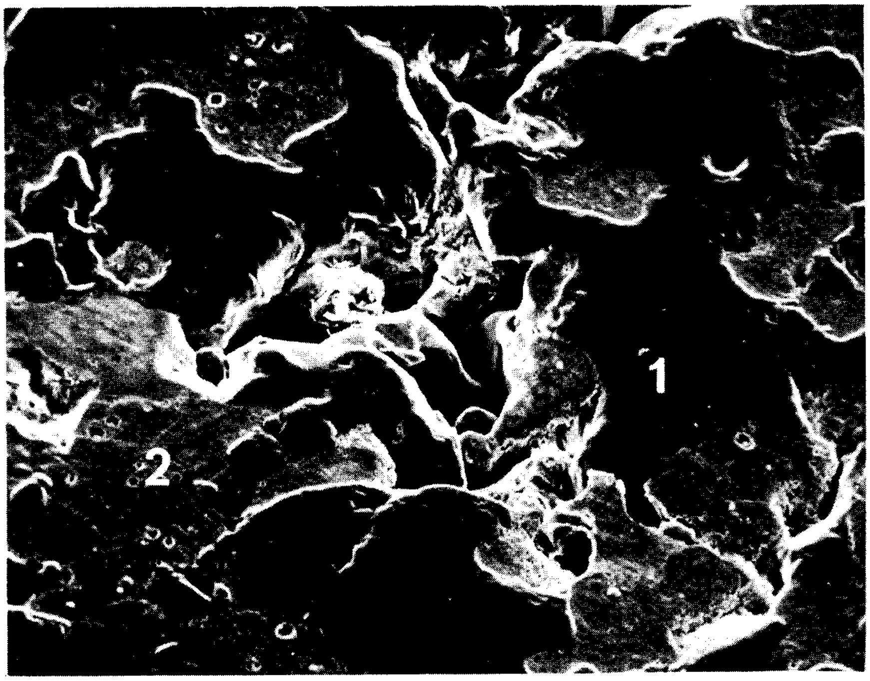

Figure 13. Magnification of Area Indicated in Figure 12

VI. CONCLUSIONS AND RECOMMENDATIONS

Operation of the laboratory-scale glass melter has proven that ICPP zirconia calcines can easily be melted by joule heating to form a homogeneous, low viscosity, leach resistant glass. The 1.5 l melter can be fed up to 1000 g at rates up to 30 g/min and can pour glass as rapidly as 155 g/min to produce 400 ml cans of quality glass.

The high-chrome K-3 refractories contain the glass melt effectively and reliably without maintenance. Fluoride volatility and corrosive attack on the refractories should not be significant for a 2-3 year melter operating lifetime.

Corrosion and phase separation of the Inconel 690 electrodes may reduce their useful lifetime by spalling if the melter is thermally cycled. This should be further investigated for vitrification of ICPP zirconia calcines. Corrosion penetration rate increases with calcine content, though it should be tolerable by using massive electrodes. Air-cooling of electrodes can reduce the corrosion rate.

Temperature control of multiple melting chambers (or multiple electrode pairs in a large chamber) must be carefully balanced. The preferential heating of low resistance-high temperature conductive paths in the glass must not be allowed or the system may overheat. The laboratory-scale melter has shown that with careful adjustment single control over two pairs of electrodes can work, but independent control for each pair is recommended.

A pilot-scale melter will be built to verify the process on a larger scale, and provide operating experience and data for a full-scale design.

VII. REFERENCES

1. R. E. Commander et. al., Operation of the Waste Calcining Facility with Highly Radioactive Aqueous Waste, Report of the First Processing Campaign, AEC-IDO-14662 (June 1966).

2. Alternatives for Long-Term Management of Defense High-Level Radioactive Waste, ERDA 77-43 (September 1977).

3. D. Gombert, H. S. Cole, J. R. Berreth, Vitrification of High-Level Calcined Wastes, DOE-ICP-1177 (February 1979).

4. Daniel Plung ed. Technical Quarterly Progress Report, April 1-June 30, DOE-ENICO-1033 (not yet published).