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Corrosion Experience in Nuclear Waste Processing at Battelle Northwest

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SUMMARY

The objective of this report is to present experience gained at Battelle-Northwest with corrosion in nuclear waste processing. The main emphasis is on corrosion as it related to the waste storage canister. Most of the canister corrosion work has been conducted in support of the In-Can Melter (ICM)(1) vitrification system. Thus, for this work we will assume the canister goes through the ICM process and is then stored in a water basin.

Three important corrosion effects act on the canister:

- Attack from the melt and melt vapors during processing
- Canister oxidation by air during processing
- Stress corrosion cracking during interim storage.

The most severe corrosion effect we have seen is oxidation of stainless steel surfaces in contact with gases containing oxygen during processing. The processing temperature is near 1100°C and the furnace atmosphere, used until now, has been air with unrestricted flow to the furnace. The oxidation rate at 1100°C is 15.8 g/cm^2 for 304L SST. Techniques for eliminating this corrosion currently being investigated include the use of different materials, such as Inconel 601®, and the use of an inert cover gas.

Corrosion due to the waste melt is not as rapid as the air oxidation. This effect has been studied quite extensively in connection with the development of a metallic crucible melter at Battelle. Data are available on the corrosion rates of several waste compositions in contact with various materials. Long-term compatibility tests between the melt and the metal have been run. We have

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found the corrosion rates due to the melt or its vapor do not pose a serious problem to the waste canister. However, these rates are high enough to preclude the practical use of a metallic melter.

Interim water storage of the canister may be a problem if proper corrective measurements are not taken. The canister may be suseceptible to stress corrosion cracking (SCC) because it will be sensitized to some extent and it will be nearly stressed to yield. The most favorable solution to SCC involves minimizing canister sensitization and stress plus providing good water quality control. It has been recommended to keep the chlorine ion concentration below 1 ppm and the pH above 10. At these conditions no failures of 304L are predicted due to SCC.(2)

We have concluded that corrosion of a canister used during the In-Can Melter process and interim storage can be controlled. Future work will concentrate on minimizing the corrosion resulting from these three mechanisms. The techniques selected will be a compromise between the corrosion effects and the other process parameters.

INTRODUCTION

Studies on the corrosion of nuclear waste storage canisters have been conducted in support of Battelle-Northwest's Nuclear Waste Fixation Program. This program is directed toward developing processes to convert high-level liquid wastes (HLLW) to borosilicate glass for final disposal. The advantages of this glass waste form are well presented by Ross and Mendel.(3) The corrosion work on waste canisters has been conducted largely in connection with the in-can melting progress. In Figure 1, the in-can melter is shown connected to the spray calciner. This progress has been selected for use at a U.S. commercial fuel reprocessing plant. The heated wall spray calciner(4) converts HLLW to calcine which is then fed directly into the in-can melter along with a glass-forming frit. The in-can melting process uses the storage canister as the melting crucible to vitrify the mixture of calcined nuclear waste and glass-forming frit. When the canister has been filled with the waste glass it will be removed from the furnace and a cap will be welded on. After inspection the canister will be placed in the interim storage water basin. In addition to acting as the melting crucible, the canister also provides protection for the glass product, acts as a barrier to dispersion, and provides a means for handling the glass block.

The investigation of the corrosion effects of waste processing on various metals was started originally to select a material for the metallic melter. This melter was used as a large crucible to melt the calcined waste and frit together. The melt was then drained into a storage canister. The best material available was Inconel 690®, but its corrosion rate was still judged to be too high for

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HLLW VITRIFICATION CONCEPT USING SPRAY CALCINER AND IN-CAN MELTER

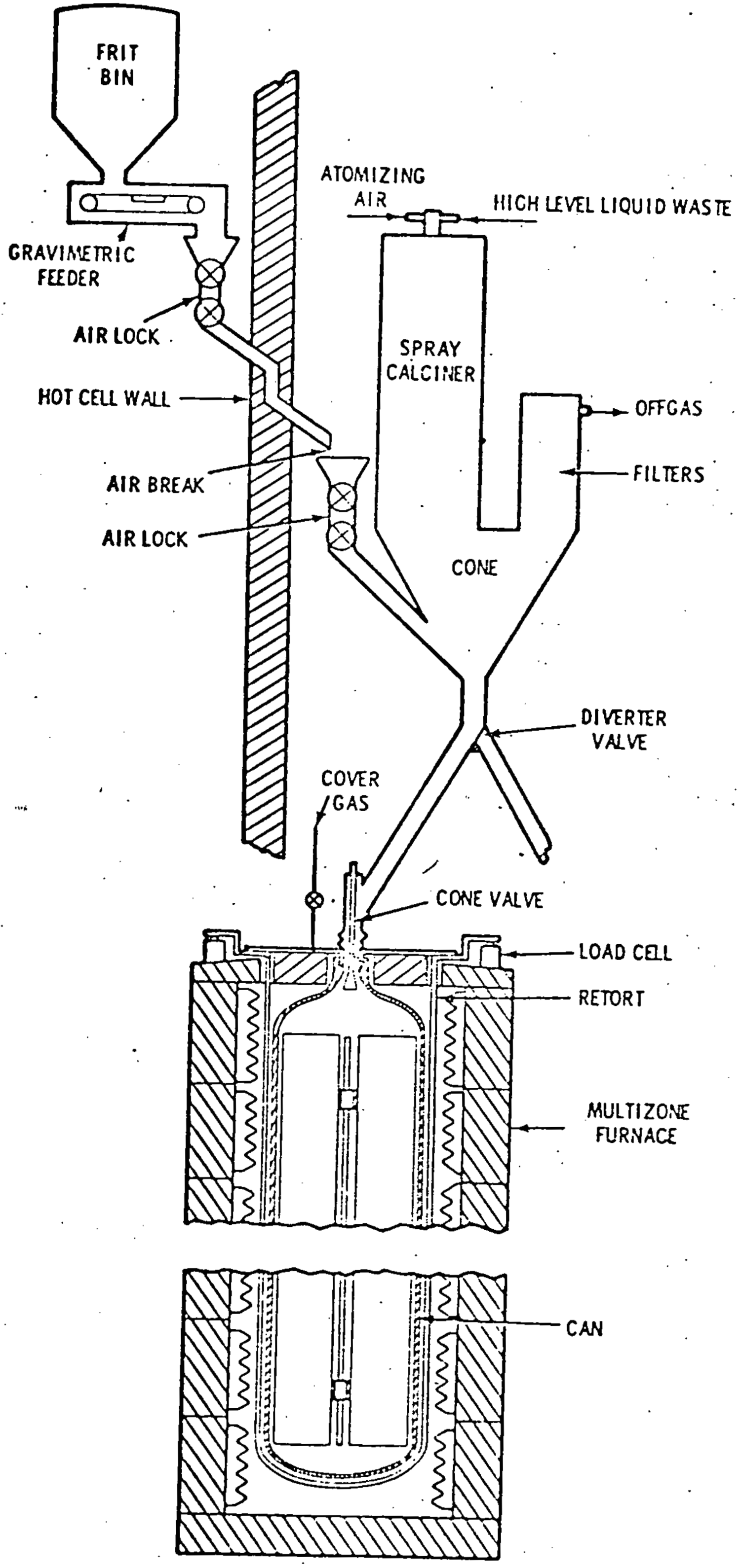

Figure 1

the melter to be of practical use. The experience and results from this work have been very helpful in the corrosion studies for the ICM canisters.

In this paper, we will discuss our experience and laboratory results concerning the corrosion of waste canisters. The paper will be divided into three sections, which will discuss the three separate corrosion effects of the melt and its vapor, the furnace air, and the water basin. In each section we discuss the corrosion mode, laboratory test procedures and results, techniques for reducing the corrosion, and anticipated future work.

To be
expanded

CONCLUSIONS

We have found that the corrosion effects of the melt, the furnace air, and the water basin on a canister used in the In-Can Melter process are insignificant or can be controlled. Methods to prevent these corrosion effects are known and will be evaluated as to their effectiveness. Future work ~~will~~ should be directed toward meeting these goals.

- Select the canister material that best meets the corrosion and other process requirements.
- Develop and evaluate methods for the control of oxidation of canister surfaces exposed to an oxygen containing atmosphere.
- Develop and evaluate methods for the prevention of stress corrosion cracking.

THE THREE MODES OF CORROSION

The tests that we have run in evaluating the corrosion rates of materials have been based on what conditions the canister will experience during its operating life. The empty canister will be placed in the ICM furnace and heated to 1075°C. The upper portion of the canister will be outside the furnace and will average about 250°C during a run. The canister is held at temperature for up to 48 hours while it is being filled. When filled, the canister will be removed and cooled at an undetermined rate. The rate is unknown because we are still evaluating different cooling rates and their effects on the canisters and the glass. It will be capped, inspected, and then sent to the interim storage water basin, where it may be held for a maximum of 10 years. The water in the basin will be at 55°C and will have good quality control.

OXIDATION OF EXTERNAL SURFACES

Corrosion due to oxidation of the surfaces in contact with an oxygen containing atmosphere is potentially of greatest concern. Rates up to 1.7 mm/day have occurred on exterior surfaces of 304L SST canisters heated to 1075°C in air. (Rates have been found using engineering scale canisters.) The importance of oxidation is not only loss of material but also a significant waste stream of spalled off material is being produced. The scale remaining on the canister also makes decontamination more difficult and may provide crack initiation sites when stored in water. Some oxidation of the canister is needed though, to give a slightly blackened surface which has a high emissivity for good heat transfer in air.

We are now investigating two methods of reducing oxidation. The first is to replace 304L SST, which has been used because it is inexpensive and is used extensively in nuclear equipment, with a higher allow metal. Inconel 601 and Incolloy 802® are two alternative materials now being investigated. Figure 2 shows the performance of these two alloys in comparison to 304 and some other alloys. Using either 601 or 802 allows the use of significantly higher operating temperatures which have process advantages, while still having little oxidation. The second method is to protect the surface of 304L. Two methods for doing this are flooding the furnace with an inert gas such as argon or coating the canister with a non-oxidizing material. We have demonstrated a plasma sprayed coating of zirconia on the surface of the canister to be effective in preventing oxidation.(5)

FIGURE 2.

CORROSION IN THE WATER BASIN

The main corrosion mechanism predicted for water basin storage of a waste canister is stress corrosion cracking (SCC). We have been performing laboratory work and studying the literature to evaluate this mechanism. The canister is susceptible to SCC because it will be sensitized and the surface will be in

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tension. Sensitization and stress inducement in the canister wall is inherent in the ICM process.

Tensile stress in the canister is caused by the glass restraining the canister from contracting during cooling in the range of 500°C to 50°C. This is because, in this range, the mean linear coefficient of expansion for 304L is 18×10^{-6} °C^{-1} and for glass is 9×10^{-6} °C^{-1}. Residual stress measurements made on a canister indicate 30 kpsi hoop stress and 36 kpsi axial stress. Calculations confirm these results. We are planning to evaluate several techniques to relieve stress in the canister wall: 1) quenching the canister to contract the metal while the glass is still yielding, 2) cooling the can to a low enough temperature to cause sufficient yielding that it would be unstressed when warmed back to normal storage temperatures, 3) placing a crushable liner between the glass and can wall, and 4) annealing the borosilicate glass at the proper temperature to produce densification. Preliminary results from quenching a canister and then heating it to densify the glass show stress levels decreased by a factor of two. The quenching operation does fracture the glass, with 96% of the glass greater than 4 mesh and only 0.01% smaller than 80 mesh.

We have evaluated the tendency of various canister materials to sensitize during processing as well as the likelihood of these materials cracking when stored in a water basin. We have made tests in the lab to substantiate sensitization values found in literature and to find information on new alloys. We have also evaluated sensitization of canisters from hot and cold engineering scale runs.

The laboratory evaluation was done on three types of stainless steel and two nickel base alloys. The specimens were fabricated from 304L, 304, 321, Incolloy 800, and Inconel 600 and were exposed at 238, 427, 538, and 705°C. Exposure times ranged from one to >10,000 hr. The degree of sensitization produced by the heat treatment was determined by exposures to boiling 65 wt% HNO_3 or, for Inconel 600, to boiling H_2SO_4 - $Fe_2(SO_4)_3$ solution. Also, U-bend specimens were fabricated from the exposed coupons and then exposed to air-saturated water at 80°C containing 100 ppm chloride to determine the propensity for stress corrosion cracking.

Table 1 gives the sensitization data, as determined by Huey tests. One or more of the heat treatments resulted in extreme sensitization of 304, Incolloy 800, and Inconel 600. Sensitization of 321 was relatively mild, whereas sensitization of 304L was somewhat more severe. Failure occurred in 2 weeks with the 304 and 304L U-bend specimens that were subjected to a heat treatment at 1000°F for 10 and for 100 hr. No other failures occurred after 9 weeks of exposure even though other specimens showed a much higher degree of sensitization. During the last four exposure weeks, the pH of the test solution was changed from 7 to 4 by adding potassium acid phthalate. The Inconel 600 specimens were not expected to crack because their nickel content is above 45% which is the point above which there is an apparent immunity to SCC. Along with measuring the tendencies to sensitize, we have looked at methods to prevent SCC.

We are in the process of evaluating three methods of preventing SCC in addition to that of reducing canister stress levels. These methods are:

- Use a material that will either not sensitize or is not susceptible to SCC.
- Provide good water quality control in the storage basin.
- Use surface treatment before or after processing.

Our past work has been concerned with using stainless steels with low carbon content like 304L or with elements added to stabilize the carbon such as 347. New work is just starting on evaluating materials with high nickel content (>45%) such as Inconel 601. These materials are generally considered immune to SCC and have other benefits over stainless steels, like oxidation resistance and greater high temperature strength.

Table 1

TABLE . Huey Tests of Candidate Canister Alloys After Heat Treatment: Corrosion Rates in Boiling 65% Nitric Acid(a)

Heat Treatment	304 L	304	321	Inc 800	Inc 600(b)
1) As mill annealed	0.5	0.7	1.8	0.2	28
2) 1 hr at 705°C	12.7	100(d)	2.6	100(d)	62
3) 10 hr at 705°C	12.9	100(d)	2.8	12.1	2000(c)
4) 100 hr at 705°C	17.2	100(d)	4.3	1.7	4000(c)
5) 1 hr at 538°C	0.5	0.8	2.1	0.2	39
6) 10 hr at 538°C	0.7	0.8	2.5	0.2	52
7) 1000 hr at 538°C	6.0	8.2	3.7	2.9	53
8) 100 hr at 427°C	0.5	0.7	2.3	0.2	22
9) 1000 hr at 427°C	0.6	0.8	2.8	0.4	22
10) 10,000 hr at 427°C	---	---	---	---	---
11) 100 hr at 238°C	0.5	0.8	2.4	0.3	26
12) 1000 hr at 238°C	---	---	---	---	---
13) 10,000 hr at 238°C	---	---	---	---	---

(a) Average of (five) 48-hr exposures
(b) 24-hr exposure to boiling 50% H_2SO_4 containing 40 g/ℓ $Fe_2(SO_4)_3$
(c) 3-hr exposure
(d) Specimen consumed before test was completed

The control of the water quality in the basin appears to provide a very good means of preventing SCC, even in partially sensitized materials. From published literature and laboratory tests we have concluded that the probability of 304L cracking during 10 yr of water storage can be nearly eliminated by controlling two water conditions: 1) maintain the chloride content of the water below 1 ppm through the use of ion exchangers, and 2) maintain a pH of 10 by addition of ammonia. [Stainless steel exposed to this environment appears to form a protective film which enables it to resist SCC for a prolonged period of time under adverse (500 ppm Cl, pH 6-8) conditions.]

We are evaluating several methods of surface treatment to prevent SCC. Literature suggests that shot-peening the canister after processing will help by placing the surface in compression.(7) We plan to evaluate this in lab and engineering scale tests. If an oxidizable material is used in processing, scale removal will be desirable from the standpoint of eliminating crevices in the scale which serve as concentration points for chloride. We have started studying electron polishing techniques as a way of removing scale as well as decontaminating the surface. This process should also smooth out sharp crevices and points in the base metal. First indications are that it is possible to remove the scale with this process. Treatments before processing, such as coatings, have been looked at. For example, mild steel was evaluated in an accelerated test. The test was performed by placing a specimen in air sparged, 80°C water which contained 100 ppm chloride. The Alonized layer was penetrated by pitting in one week.

We have had experience of one canister failing via a cracking mechanism. The canister was made of 310SS and contained radioactive waste from the WSEP Program.(6) The canister was stored one year in water, followed by 3 1/2 yr of air storage at 400°C, and then 10 months in water at 50°C, which was when the failure occurred. The water showed high amounts of dissolved oxygen and 13 ppm chloride. A Huey test was run on samples from this canister along with samples from a 304L canister which had been stored in air for 2 years at 400°C. The results, given in Table 2, show that both samples were evently sensitized. The samples had weight losses representing a uniform penetration rate of 40 mil/month. Micrographs indicate gross intergranular cracking near the fracture area. Intergranular cracking is indicative of stress assisted cracking, not stress corrosion cracking. Areas free of macrocracks were also free of microcracks. Figure 3 has a picture of the inside and outside edge of a piece in the area of the crack.

Table 2.

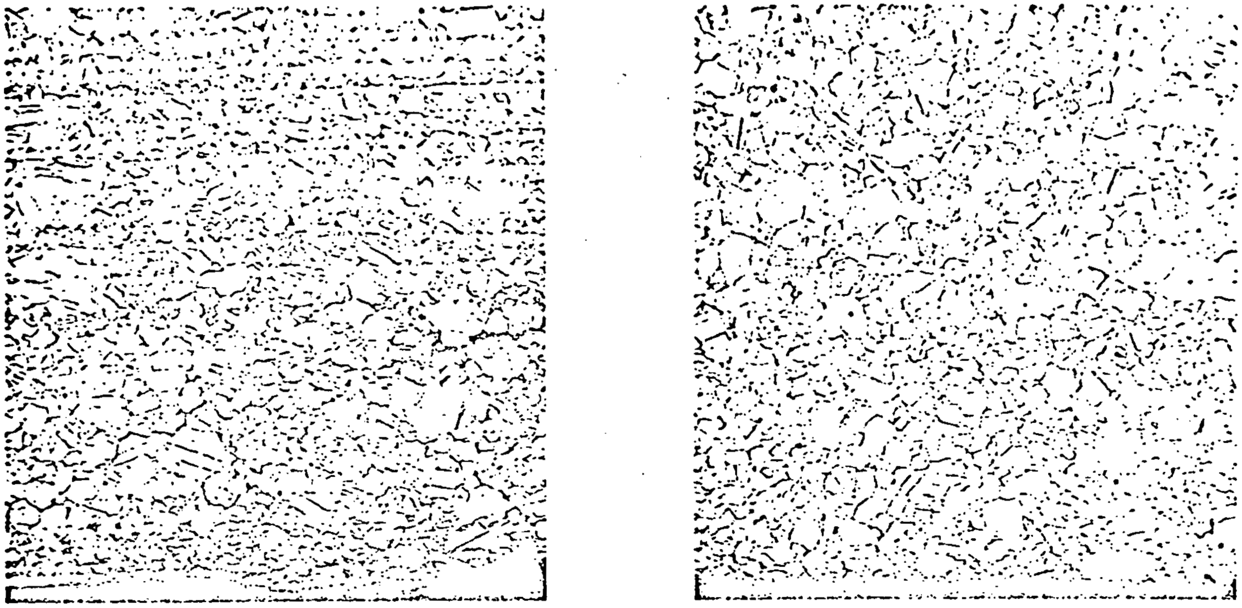
TABLE ___. Huey Test Data

Material	Corrosion Rate, mils/month(a)					
	Period					
	1	2	3	4	5	Avg
304L(b)	57	155	170	168	154	141
310(c)	45	180	207	222	209	173

(a) The maximum rate for acceptable material is usually 2 mil/month (average).

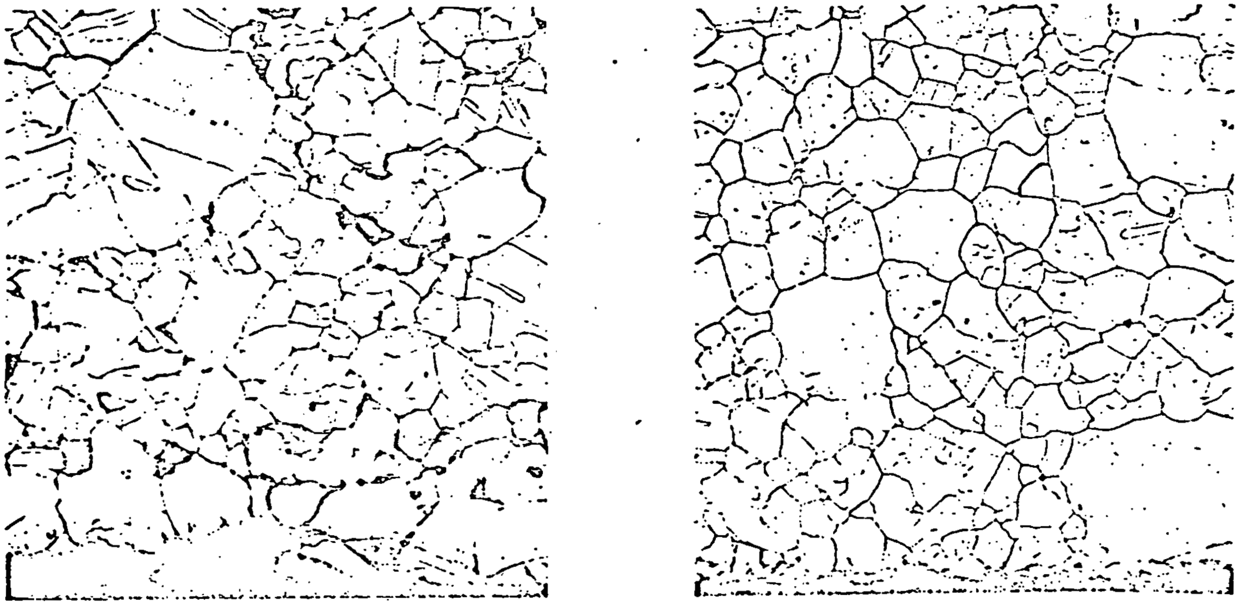
(b) 304 specimen from WSEP SS-8 canister. One year in water, two years in air at 400°C.

(c) 310 specimen from WSEP SS-9 canister. One year in water, 3.5 years in air at 400°C, 10 months in water at 50°C.



Internal Surface Edge 75X

External Surface Edge 75X



Internal Surface Edge 225X

External Surface Edge 225X

FIGURE 3 ~~14~~. Photomicrographs of Canister Wall Section from WSEP Canister 36--Sample Area #1 (Oxalic Acid Electrolytic Etch)

The cracking of this canister was not unexpected; the canister was stored under very adverse conditions and was severely sensitized. Canisters of 304L, taken directly from the ICM furnace, have much lower Huey Test corrosion rates. The maximum corrosion rate for samples taken from the walls of these canisters was 1.15 mil/month and samples from the neck were 9.1 mil/month. The means, under the operation conditions seen at this time for the ICM melter, sensitization of any importance exists only in the neck. This will not always be true in every case and not if the process steps change.

CORROSION EFFECTS OF THE GLASS MELT

The effects of vitrified nuclear wastes and of the vapor from the melt have been relatively unknown. In order to make material selections for pieces of process equipment we had to perform extensive laboratory tests. We have found that the apparent corrosiveness of the melt is not as severe as we had first suspected. Corrosion rates less than 10 mil/hr have been measured for several waste compositions, in contact with a variety of metals, at temperatures above 1100°C.

Our work on this matter has been somewhat evolutionary in nature. As the work proceeded, new waste and frit compositions were developed as well as new processes. The new compositions often brought in new corrosive elements whose effects had to be evaluated. The new processes brought changes in operation conditions such as temperature, time in contact with the melt, and strength needs.

The first process looked at was the metallic melter. This melter received calcine and frit, melted them together, and then dumped the batch into a canister. The melter required good corrosion resistance at temperatures above 1100°C for long periods of time. In contrast, the in-can melting process required good high temperature corrosion resistance for only several days. The ICM process also required materials with high temperature strength, resistance to corrosion in water, and low cost. The work on these processes was not exclusive, which means data on materials evaluated for the metallic melter can be applied to the ICM process.

Three basic melt compositions were used in the majority of the work. The compositions are based on the predicted composition of the actual waste, with substitutions made for expensive compounds. The glass forming frit used for the three wastes was called 73-1. Its composition is given in Table 3. The frit was mixed with the different wastes in ratios of 2:1 to 3:1. Table 5 gives the composition of PW-4b waste and 73-1 frit, and the resulting glass. The other two wastes were essentially the same except for changes in several constituents. PW-6 and PW-7a have higher concentrations of Na_2O, Fe_2O_3 and U_3O_8, which reflect the fact that these compositions are combinations of high and intermediate level wastes. In this report, we will use the waste number to indicate a melt composition of three parts 73-1 and one part waste.

Table 3. Composition of Simulated PW-4b Waste, 73-1 Frit, and Resulting Glass Used for the WFP.

Constituents	Weight Percent of Total Oxides		
	PW-4b Waste	73-1 Frit	72-68 Glass
K_2O for Rb_2O	0.49	5.5	4.18
SrO	2.90	2.0	2.24
Y_2O_3(a)	0.07		0.02
ZrO_2	13.54		3.56
MoO_3 for Tc_2O_7	17.48		4.60
Fe_2O_3 for RuO_2	9.02		2.38
Co_3O_4 for Rh_2O_3	0.83		0.22
NiO for PdO	2.86		0.75
Ag_2O	0.24		0.06
CdO	0.27		0.07
TeO_2	1.99		0.52
Cs_2O	7.89		2.08
BaO	4.29	2.0	2.60
La_2O_3(a) for Nd_2O_3	8.50		2.24
CeO_2(a) for UO_2	17.00		4.48
Pr_6O_{11}(a)	1.77		0.47
Nd_2O_3(a)	6.02		0.16
Sm_2O_3(a)	1.06		0.28
Gd_2O_3(a)	0.71		0.19
Na_2O	-	5.5	4.06
Cr_2O_3	0.94		0.25
P_2O_5	1.84		0.48
SiO_2		37.0	27.28
B_2O_3		15.1	11.13
ZnO		28.9	21.31
CaO		2.0	1.47
MgO		2.0	1.47
Kilograms/MTU	36.4	72.9	109.3

(a) From natural rare earth mixture

The work with the metallic melter demonstrated the resistance of a variety of alloys under extreme melt conditions. Specimens of 15 commercial alloys were placed in PW-6 melt at 1150°C for 425 hr. The compositions of the alloys and the test results are given in Tables 4 and 5, respectively. A second test (results in Table 6) was run on the seven best performing materials to demonstrate the effect of temperature on the corrosion rate. Inconel 600 and 601 which have been chosen as possible canister materials, have good corrosion resistance.

Also at this time, we evaluated three elements that were suspected to possibly accelerate corrosion. These three elements were ruthenium, lead and zinc. Ruthenium is a fission product that occurs in all wastes, and lead and ~~bad~~ zinc provide desirable physical properties to the glass. In the cases of the Ru and Zn containing melts (Table 7 and 8) the corrosion rate was not severely affected and there was no preferential attack. The melt containing lead was found to be very corrosive (see Table 9). Corrosion by the melt on Inconel 601 and 20-45-5 was catastrophic and at the melt-vapor interface was severe for all the cases.

When emphasis was shifted from the metallic melter to the In-Can Melter process, new criteria came into the material selection process. We started tests on materials that were hoped to be corrosion resistance along with being inexpensive. Samples were run for 100 hr in the PW-4b melt. Table 10 shows the materials, the melt temperature, and the results from the test. The specimen of 401 SS failed catastrophically in both the melt and the melt vapor.

Two other materials were evaluated as a canister material. A specimen of mild steel was flamed sprayed with 30% Al_2O_3 - 70% NiAl and was then exposed for 24 hr at 1050°C to PW-7a melt. The material experienced severe corrosion ($\sim$2 mill/hr) at the melt-vapor interface and in the vapor phase. A specimen of alonized mild steel was exposed for 24 hr at 1100°C to PW-7a melt. The part of the specimen exposed to the melt was severely corroded, losing the alonized layer and 28% of the metal. An uncoated piece of mild steel was exposed at the same time and it was attacked catastrophically in the vapor phase. The penetration rate was found to be about 100 mils/hr.

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Table ~~3~~ 4. Nominal Composition of Candidate Melter Alloys

Alloy	Weight Percent Cr	Ni	Mo	Fe	Others
Corronel 230	35	65	--	--	
316 SS	16	12	3	bal	
329 SS	25	5	2	bal	
309 SS	22	13	--	bal	
E-Brite 26-1	25	--	--	bal	
Owens-Corning Alloy	26	bal	--	3	6 W
20-45-5 Alloy	20	45	5	bal	
Inconel 601	23	60	--	14	1 Al
Inconel 617	22	54	9	--	1 Al, 12.5 Cr
Inconel 690	30	60	--	10	
Inconel X	15	bal	--	8	2 Ti, 1 Al, 1 Nb
RA 333	25	45	3	bal	3 W, 3 Co
Hastelloy X	22	bal	9	18	1 W, 2 Co
18-18-2 Alloy	18	18	--	bal	2 Si
Supertherm	25	35	--	bal	14 Co, 5 W
Udimet 710	18	bal	3	--	15 Co, 1.5 W, 5 Ti, 2.5 Al

Tabl 5 - ~~TABLE 5.~~ Corrosiveness of Waste Melt to Candidate Melter Alloys at 1150 °C

Melt Composition: 100 g calcine, 64 g SiO_2, 42 g H_3BO_3, 100 g $Al(NO_3)_3$, 40 g $CaCO_3$

425 hour exposures in alumina crucibles

Alloy	Corrosion Rate, mils/mo Liquid	Interface
Corronel 230	2.1	2.3
316 SS	dissolved	dissolved
329 SS	6.7	--
309 SS	7.4	10.6
E-Brite 26-1	6.7	--
Owens Corning Alloy	4.9	6.1
20-45-5 Alloy	2.7	2.9
Inconel 601	6.5	5.6
Inconel 617	6.3	5.3
Inconel X	5.5	6.7
RA 333	9.9	13.0
Hastelloy X	5.4	6.0
18-18-2 Alloy	20.6	62.4
Supertherm	19.8	--
Udimet 710	27.4	32.3

TABLE ~~7~~ 6. Corrosiveness of Waste Melt as a Function of Temperature

Melt Composition: 100 g PW-6 calcine, 64 g SiO_2, 42 g H_3BO_3, 100 g $Al(NO_3)_3 \cdot 9H_2O$, 40 g $CaCO_3$ 165 hour exposure in alumina crucibles

Alloy	Corrosion Rate at 1150 °C, mils/mo		Corrosion Rate at 1200 °C, mils/mo	
	Melt	Interface	Melt	Interface
Hastelloy X	5.4	6.0	24	28
Corronel 230	2.1	2.3	4.9	6.1
Inconel 617	6.3	5.3	21	32
Inconel 601	6.5	5.6	17	18
Inconel 690	3.5	2.1	4.3	5.4
Inconel 600	7.2	8.5	-	-
Inconel 804	5.9	—	—	—
50 Cr - 50 Ni	5.1	3.5	-	-

TABLE ~~8~~ 7. Corrosiveness of Zinc-Bearing Waste Melt

Melt Composition: 6.85 g PW-4b calcine, 6.70 g H_3BO_3, 6.80 g SiO_2, 2.77 g $NaNO_3$, 2.17 g KNO_3, 15.72 g $Zn(NO_3)_2 \cdot 6\,H_2O$, 0.66 g $CaCO_3$, 2.34 g $Mg(NO_3)_2 \cdot 6H_2O$, 0.75 g $Sn(NO_3)_2$, 0.63 g $Ba(NO_3)_2$.

Exposure in alumina crucibles for 283 hours at 1150 °F.

Alloy	Corrosion Rate, mils/month	
	Melt	Interface
Inconel 690	1.4 (a)	1.9 (a)
Inconel 600	7.5 (a)	13.2 (b)
20-45-5	7.8 (a)	3.5 (a)

TABLE ~~4~~8. Corrosiveness of Ruthenium-Bearing Waste Melt

Melt Composition: 100 g PW-6 calcine, 64 g SiO_2, 42 g H_3BO_3, 100 g $Al(NO_3)_3 \cdot 9H_2O$, 40 g $CaCO_3$ and one wt. percent Ruthenium added as $Ru(OH)_3$.

Exposure in alumina crucibles for 165 hr at 1150 °C.

Alloy	Corrosion Rate, mils/mo	
	Melt[a]	Interface[a]
20-45-5	10 (2.7)	9.6 (2.9)
Corronel 230	4.8 (2.1)	3.3 (2.3)
Inconel 690	2.9 (3.5)	1.9 (2.1)

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[a] Parenthetical numbers are values determined in similar tests in the absence of ruthenium.

TABLE ~~5~~9. Corrosiveness of Lead-Bearing Waste Melt

Melt Composition: 100 g PW-4b calcine, 266 g $PbSiO_3$, 58 g KNO_3, 96 g SiO_2.

Exposure in alumina crucibles at 1150 °C for 150 hours.

Alloy	Corrosion Rate, mils/mo	
	Melt	Interface
Inconel 690	12	26[a]
50 Cr - 50 Ni	6.7	41[a]
20-45-5	83	dissolved
Corronel 230	7.0	24[a]
Inconel 601	dissolved	dissolved

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[a] Severe attack at melt-vapor interface area.

TABLE ~~8~~ 10. Corrosion Rates Pertinent to In-Can Melting

Conditions: Corrosion specimens exposed to liquid and vapor phase of melt prepared from PW-4b calcine (1 part) and frit 73-1 (2.8 parts) for 100 hr at indicated temperature.

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Material	Melt Temp. °C	Corrosion Rate, mils/month	
		Melt	Vapor
304L	950	3.2	4.5
310	950	1.7	1.0 pitting
304L	1000	15 pitting[a]	8.8
310	1000	1.8	5.1
410	1025	dissolved	disintegrated
Inc 600	1050	7.6	4.6
Inc 601	1050	4.0	3.8
Inc 690	1050	2.5	2.5
18-18-2	1050	38	2.0
Incoloy 804	1050	2.7	3.1
Multimet	1050	2.0	disintegrated

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a. About 5 mils deep

As more emphasis was placed on the ICM process, the need became greater to select some materials for extensive evaluation as canister materials. The first material selected was 304L SS. This material was selected because it has wide use in the nuclear industry along with fair corrosion resistance and low susceptability to SCC. The majority of all work pertaining to ICM canister has been done with 304L. We have now started to evaluate other alloys such as Inconel 601 and Incolloy 802 in more detailed laboratory work and on an engineering scale. The composition and properties of these materials are presented in Table 11.

ALLOY	FE	CR	NI	MO	THERMAL CONDUCTIVITY BTU/HR FT °F	THE EXP IN/IN
304L	BAL	18	8	--	12.2	1
INCOLOY 800	46	20	32	--	10.6	
INCONEL 600	8	16	72	--	12.1	
E-BRITE 26-1	BAL	26	--	1	11.3	

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We have determined the corrosion rate of 304L as a function of temperature. The test used the PW-46 melt at the temperature and time shown in Table 12

Table 12

Corrosion Rates of 304L Pertinent to In-Pot Melting

Jan '75

USE

Melt Temp., °C	Exposure Hours	Corrosion Rate, mils/mo Melt	 Vapor
950	100	3.2	4.5
1000	100	15 (2.4)	8.8 (15)
1050	150	118	35
1100	66	90	64
1150	24	Consumed >3750	760

Tests Dakan initiated PW4b

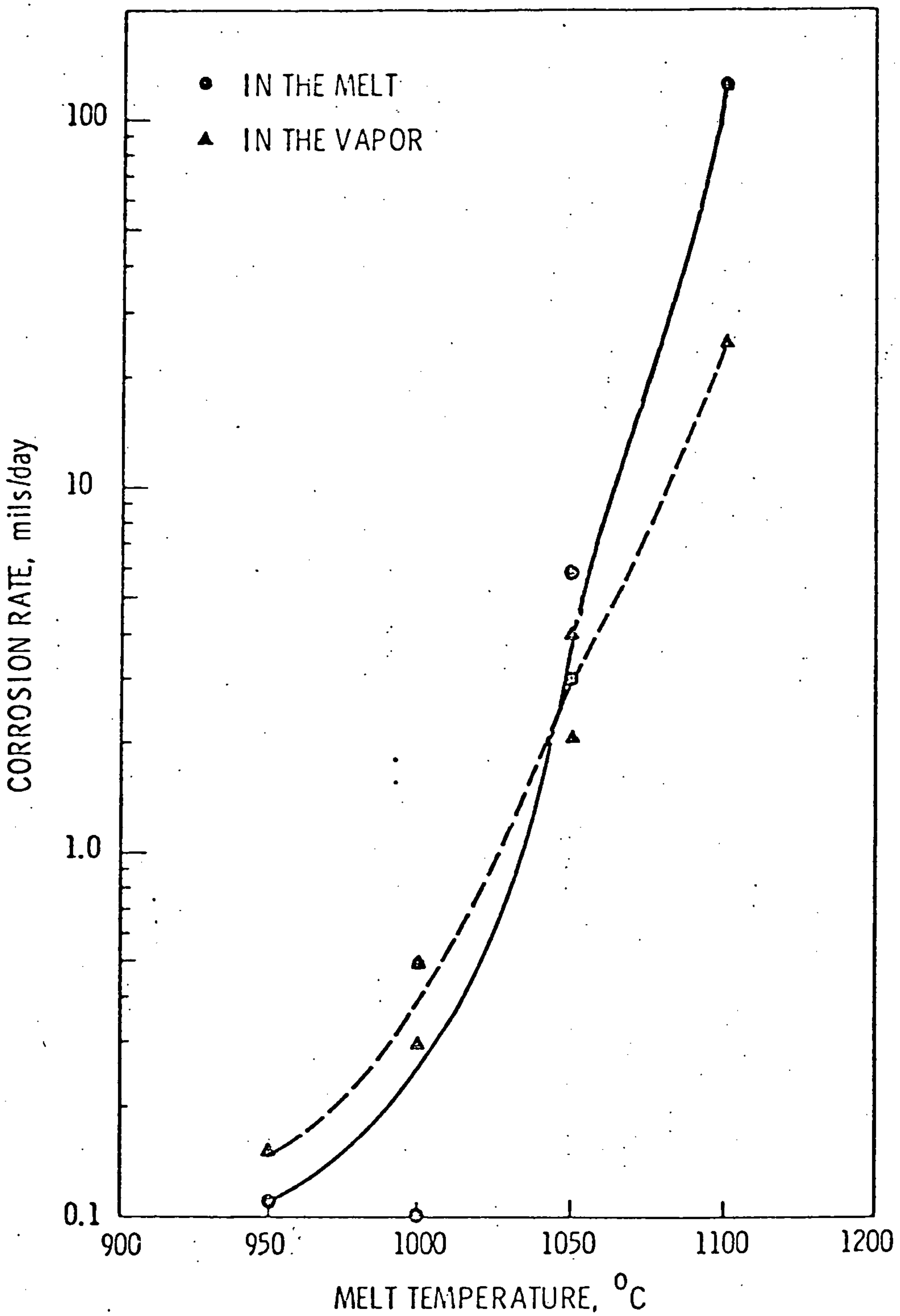

Figure [illegible] 4 ?
Corrosion Rate of 304L Stainless Steel in
Simulated Nuclear Waste Glass Melt

Where is this
called
out?

One should note the very rapid increase in corrosion rate as the temperature exceeds 1050°C.

In addition to short term tests to evaluate corrosion during processing we have also looked at the long term effects. We have a glass compatibility test going using PW-7a melt in 304L SS, Incolloy 800, and Inconel 600. There are 35 capsules, each containing a corrosion coupon. The capsules are being held at 250, 550 and 700°C for exposure periods ranging from one month for capsules at 700°C to 2 years for those at 250°C. Table__ gives the program planned for this test. Results are available only on specimens exposed at 1300°F for 1 month. Table __ gives the corrosion rates as determined by weight loss of the coupons. It appears from the results there is no problem with long term glass corrosion of the canister unit. Another test was run exposing 304L to PW-4 calcine containing water. The samples were held at 60, 90 and 300°C for 9 months. Attack was negligible for all cases run (~0.05 mill/yr).

Another phase of attack we looked at was from contamination in the melt and from new chemical additions used to improve the quality of the glass. Corrosion tests were made with 304L to determine the effect of chloride and fluoride additions to the PW-7 melt. With chloride and fluoride additions at the 1% level (as NaCl and NaF), and with a melt temperature of 1000°C, corrosion rates were 2.1 and 17.4 mils/month, respectively. A control specimen corroded at a rate of 2.4 mils/month. Intergranular attack was evident only on the specimen exposed to the fluoride-bearing melt. A substance (probably $MoOCl_3$ and/or $ZrCl_4$) was volatilized from the chloride-bearing melt; the terminal chloride content was probably very low.

The addition of silicon metal to the melt to prevent molybdenum from forming a soluble second phase material caused concern on what would be released by the reducing action. It was discovered Ru and Zn metal was released as a vapor so we ran tests to determine if embrittlement of the canister wall would occur. Tests were run using 1.5% silicon metal in PW-7a melt at 1050°C. No loss of ductility was noted with only a slight increase in the general corrosion rate.

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Omit type yet,

CAPSULE TYPE COMPATIBILITY TESTS

Waste Form	Temp °~~F~~C	Capsule Material	Capsule Condition(1)	~~Waste~~ Glass Composition(2)	Exposure Time	No. of Capsules
~~Calcine~~	~~1300~~	~~304L, Inc. 800, Inc. 600~~	~~A.F.~~	~~F.S.~~	~~1 mo~~	~~3~~
~~Calcine~~	~~1000~~	~~304L, Inc. 800~~	~~A.F., S.R.~~	~~F.S., F.S. + Add~~	~~3 mo~~	~~8~~
~~Calcine~~	~~460~~	~~304L, Inc. 800~~	~~A.F., S.R.~~	~~F.S., F.S. + Add~~	~~1, 2, X yr~~	~~24~~
Glass	~~1300~~ 700	304L, Inc. 800, Inc. 600	A.F.	~~F.S.~~ I, ~~F.S.~~ I + Add	1 mo	6
Glass	~~1000~~ 550	304L	A.F., S.R.	F.S., F.S. + Add	3 mo	4
Glass	~~1000~~ 550	Inc. 800, Inc. 600	A.F.	F.S., F.S. + Add	3 mo	4
Glass	~~460~~ 250	304L	A.F., S.R.	F.S., F.S. + Add	1, 2, X yr	12
Glass	460 250	Inc. 800, Inc. 600	A.F.	F.S., F.S. + Add	1, 2, X yr	12
						~~72~~ 38

Notes: (1) A.F. = as fabricated; S.R. = stress relieved

(2) ~~F.S. = flow sheet~~ I = Glass I; ~~F.S.~~ I. + Add = ~~flow sheet~~ Glass I plus 2 x H_2O, NO_3^- and halogen plus 10 wt % sodium as $NaFeO_2$.

TABLE 7. ~~[illegible]~~ Compatibility Tests

Corrosion Rates at 1300°F after One Exposure Month

Material	Waste Form	Glass ~~Waste~~ Composition[a]	Corrosion Rate, mils/year
304L	Glass	A	0.6
304L		B	0.4
Inc 800		A	1.0
Inc 800		B	0.3
Inc 600		A	0.2

Conversion factor

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a. A = PW-7 ~~flowsheet~~; B = PW-7 ~~flowsheet~~ plus 100-fold increase in sodium content.