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PROCESSING RADIOACTIVE WASTE

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ABSTRACT

In the development of the phosphate glass process for conversion of highly radioactive wastes to stable solids, platinum has been used successfully for the high temperature crucible. In this application a platinum crucible has been used at temperatures of 800°C-1200°C for a total of 8000 hours with no signs of deterioration. It was demonstrated that chemical reducing conditions must be avoided; otherwise rapid deterioration of platinum may take place in the presence of molten phosphate. Tests to determine the useful life of platinum included long-term creep measurements at 1250°C. The latest results of these tests, which are still in progress, are presented. Economic factors associated with the use of platinum in high level waste processing are discussed briefly.

INTRODUCTION

In the development of processes for converting high level radioactive wastes to stable solids, by high temperature methods, platinum and its alloys are showing promise as a practical material of construction for the crucibles.

In the Brookhaven process the feed solution, prepared by addition of orthophosphoric acid to raw waste, is reduced in volume by evaporation of water and nitric acid and, upon heating to 1200°C in a platinum crucible, sulfuric acid is driven off and the concentrate converted to molten glass.

Platinum crucibles have been used in the manufacture of quality optical glasses for some years. However, the crucibles are normally supported on ceramic materials and are accessible

for inspection, repair and reclamation. In the processing of radioactive wastes, on the other hand, special methods of supporting and handling the crucible had to be devised. Little information on high temperature long-term creep strength of platinum was available in the literature, and, information on corrosion of platinum at high temperatures in the presence of phosphate and sulfate was limited.

EARLIER CERAMIC CRUCIBLE TESTS

One of the first requirements in the development of the phosphate glass process was to evaluate selected materials of construction for the crucible which would be exposed to the highly corrosive molten phosphate and the thermal stresses associated with operation at 1250°C. A considerable number of ceramics, i.e. alumina, lavite, zirconia, magnesia, chromium and tin oxides were exposed to molten phosphate glass at 1200°C for 350 hours. The specimens were then sectioned and studied under high magnification. The areas of greatest attack on these ceramics were at the gas-liquid interface and only the high purity alumina (99% Al_2O_3) showed no signs of deterioration. On the basis of this information, alumina containers, 2-1/2 in. i.d. x 18 in. long with 1/8 in. wall and bottom thickness, were used in bench-scale experiments and found to be satisfactory for the small-scale operation. Based on the successful bench-scale runs a large alumina crucible, 5 in. in diameter x 6 ft. long with a 1/4 in. wall was installed in the pilot plant. However, during the first run after 18 hours of operation a crack developed in the crucible which caused the run to be terminated. It was apparent that the crucible had cracked as a result of thermal shock possibly due to rapid heating or to the introduction of relatively cold feed.

METAL CRUCIBLE TESTS

A number of metals including tantalum, Nionel, Carpenter 20, stainless steel 304 and 316, Hastalloy B and D, and platinum were tested up to 1100°C in molten phosphate glass. These metals showed good resistance to molten glass up to 950°C but at temperatures above 1050°C the coupons, with the exception of the platinum sample, were totally destroyed within an hour. The platinum coupon showed no signs of corrosion. To extend these tests, specimens of platinum and platinum alloys were exposed to molten glass for 3000 hours at 1200°C. These samples were sectioned and studied metallographically, see Fig. 1. The top row represents specimens which had been immersed in phosphate glass while those represented in the bottom row were control samples which had been in the furnace for the same length of time. Platinum and platinum gold showed no signs of corrosion. Platinum rhodium samples showed intergranular corrosion to the extent of approximately 7.5 mils per year. The platinum iridium sample showed intergranular corrosion but the depth of penetration

was at the rate of only 2 mils per year. Since there was no apparent advantage in using platinum gold, pure platinum was selected for future use in all development studies.

The resistance of platinum to corrosion in the phosphate system is dependent on oxidizing conditions being maintained at all times. Reductants react with phosphate to give phosphorus which then combines with platinum to give low melting alloys.

To study the resistance of platinum under actual glass-making conditions, a bench-scale unit using a platinum crucible 3 in. in diameter with a 40 mil wall and 10 in. long, shown in Fig. 2, was used. Thus the crucible was exposed to melter off-gases, principally sulfuric acid, at the elevated temperatures. Several crucibles of this type were heated with both induction and resistance furnaces, through many thermal cycles wherein the temperatures were lowered sufficiently for the glass pool to solidify. Under these conditions the crucible became distorted due to shrinkage of the glass on cooling. The wall was pulled in some 1/4 in. but the crucible was entirely satisfactory for use in bench-scale experiments after some 300 cycles.

A metallographic view of the inside wall of the bench-scale crucible after 1000 hours of service is shown in Fig. 3. The wall exposed to the liquid phase and the gas phase showed, respectively, less than four microns of transgranular corrosion and no detectable corrosion. This indicated that corrosion was minimal and that platinum crucibles would be suitable for extended service.

DESIGN OF A PLATINUM CRUCIBLE

The first platinum crucible used in the pilot plant was 8 in. in diameter x 24 in. high with a 40 mil wall and was contained in a support shell of 1/4 in. Inconel 702, as shown in Fig. 4. A coating of aluminum oxide 10 mils thick on the platinum vessel served to prevent migration of nickel into the platinum at the high temperatures. After 7175 hours of use the vessel was taken out of the furnace and inspected. There were no indications of corrosion or creep.

The vessel was then replaced in the pilot plant in preparation for a new run. Shortly after start-up a continuing discharge of molten glass from the crucible occurred. Upon dismantling the furnace it was apparent that the molten glass had first seeped out of a break in the freeze valve tube 2 in. below the bottom of the crucible and migrated upward along the tube wall to the hotter zone at the base of the crucible and to a region between the Inconel 702 support vessel and the platinum crucible. The result was that considerable deterioration at the bottom of the crucible occurred as shown in Fig. 5. The chemical mechanism

by which this failure occurred involved the Inconel 702 reacting with the molten phosphate glass to produce elemental phosphorus which combined with the platinum to form a low melting alloy. The cause of the break in the freeze valve tube was attributed to the method of straightening out the tube after a sharp bend had occurred as a result of accidental dropping of the crucible. At the time of the shutdown the crucible had 7175 hours of service above 800°C of which 1375 hours were at glass-making conditions at 1250°C.

IMPROVED PLATINUM CONTAINER

A new pilot plant crucible was fabricated as shown in Fig. 6. The design of this vessel was based on an extrapolation of existing data, with low stress values and without any provision for lateral support such as the Inconel shell. The vessel is principally supported by a flange at the top and partially supported by a ceramic base plate. The new vessel has operated successfully for 8900 hours of which 1148 hours have been at 1250°C glass-making conditions.

On one occasion during a run of the phosphate glass plant a power failure permitted the crucible to cool and the glass pool to solidify. No damage was evident on inspection of the crucible as might have been expected due to the contraction of glass on cooling. In normal operation the glass is drained from the crucible before cooling, by means of the freeze valve.

EVALUATION OF USEFUL LIFE OF CONTAINER

An important consideration in testing the new vessel in the pilot plant was its mechanical strength at the high temperatures. Independent of the pilot plant studies high temperature tests (1250°C) are being made with platinum stressed at 50 and 100 psi at Battelle Memorial Institute. The results of these experiments with pure platinum after some 2000 hours are shown in Fig. 7. The test at 50 psi, shown here as a solid line, has progressed for some 2100 hours. For the first 1800 hours the creep was a total of 1.38% and for the last 300 hours it showed no creep. The test at 100 psi, shown here as the dotted line, has been in operation for 1750 hours. The results show peculiar behavior, i.e., a rapid creep rate for the first 300-400 hours followed by a negative creep. The highest point on the curve at 340 hours shows a creep total of 1.42%. However, recovery and negative creep to the extent of 0.6% occurred during the latter 1400 hours, thus giving a total creep after 1750 hours of 0.82%. These tests will be continued for another 3000 hours.

As an indication of the resistance of platinum to melter off-gases, the cover of the original crucible has shown little or no corrosion after some 13,000 hours of exposure to the gases at approximately 500-600°C.

There is some question as to the effects of migration of certain waste components into the platinum. Hot cell experiments at Battelle Northwest Laboratories revealed small penetration of fission products into platinum crucible liners several mils in thickness. These liners, used to make phosphate glass from 56 gal/ton Purex waste, were stripped from the radioactive solidified glass and repeatedly washed in HCl to remove surface activity. Successive layers of platinum were then removed by aqua regia and the cerium 144, ruthenium 106, and cesium 137 were counted by radiochemical techniques. Of the few percent of fission products found in the platinum, 90% of these were found in the first .03 mils. The results, however, are quite preliminary and more extensive experiments are required. It is not known if this is an interstitial penetration of the contaminated glass or a migration into the platinum. Brookhaven has initiated a program to determine whether there are any detrimental effects associated with waste components migrating into the platinum. Concern is mainly for compounds such as cesium and ruthenium which undergo chemical rearrangement, i.e. ruthenium dioxide undergoes an auto-oxidation-reduction at 1000°C forming ruthenium metal and ruthenium tetraoxide. It is likely that any ruthenium metal thus formed would be immediately reoxidized in the phosphate system.

The economic factor involved in the proposed use of platinum crucibles may be considered, roughly, on the basis of the amount of uranium processed in the production of the wastes. Assume a cost of \$50,000 and a 1-year service life, for a commercial-plant size crucible 8 in. diameter x 24 in. tall. Such a crucible would be adequate for processing the wastes from the reprocessing of some 1500 tons of uranium. The cost of the crucible per ton of uranium reprocessed therefore, would be \$33 for the 1-year service life and \$17 for a 2-year service life. Further assuming that eventual damage to the crucible would largely be confined to the lower 6 in. section the replacement cost would be more on the order of \$12,500 or \$8 per ton of uranium for a 1-year service life.

CONCLUSIONS

Platinum appears to be a suitable crucible material for high temperature processing of high level wastes both from the standpoint of mechanical strength and corrosion resistance.

Estimated platinum costs are very small based on the relatively large amounts of uranium reprocessed in the production of the wastes.

CORROSION OF PLATINUM ALLOYS BY PHOSPHATE GLASS AT 1200 °C
EXPOSURE TIME = ~ 3000 HOURS

IMMERSED IN
PHOSPHATE
GLASS
AT 1200°C

IN FURNACE
AT 1200°C

FIGURE 1

FIGURE 2

Platinum Crucible in Bench-Scale Unit.

IN MOLTEN GLASS

IN OFF GAS

MAGNIFICATION 250X

PLATINUM USED IN MAKING PHOSPHATE GLASS FOR 1000 hrs
AT 1200°C

FIGURE 3

PLATINUM CRUCIBLE WITH
INCONEL 702 SUPPORT SHELL

FIGURE 4

FIGURE 5

Platinum Crucible After Failure With Inconel
Shell Removed.

Improved BNL Pilot Plant Platinum Crucible.

FIGURE 7

FIGURE 8

BNWL Prototype Platinum Vessel.