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RECLAIMING SILVER FROM SILVER ZEOLITE

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ABSTRACT

Silver zeolite is used to capture radioiodines from air cleaning systems in some nuclear facilities at the Idaho National Engineering Laboratory. It may become radioactively contaminated and/or poisoned by hydrocarbon vapors, which diminishes its capacity for iodine.

Silver zeolite contains up to 38 wt% silver. A pyrometallurgical process was developed to reclaim the silver before disposing of the unserviceable zeolite as a radioactive waste. A flux was formulated to convert the refractory aluminosilicate zeolite structure into a low-melting fluid slag, with Na_2O added as NaOH instead of Na_2CO_3 to avoid severe foaming due to CO_2 evolution.

A propane-fired furnace was built to smelt 45 kg charges at 1300°C in a carbon-bonded silicon carbide crucible. A total of 218 kg (7000 tr oz) of silver was reclaimed from 1050 kg of unserviceable zeolite. Silver recoveries of 97% were achieved, and the radioisotopes were fixed as stable silicates in a vitreous slag that was disposed of as a low level waste. Recovered silver was refined using oxygen and cast into 100 tr oz bars assaying 99.8+% silver and showing no radioactive contamination.

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The process described herein is the subject of U.S. Patent 4,564,391, "Method for the Recovery of Silver from Silver Zeolite," January 14, 1986.

This report is an abridgement of "Silver Recovery from Silver Zeolite," a thesis. The original is retained by the University of Idaho, Moscow, ID. Copies of the unabridged text may be obtained from University Microfilms International, 300 N. Zeeb Road, Ann Arbor, MI, 48106.

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INTRODUCTION

Provisions to capture and retain fission products are a necessary part of any reactor safety program. There is a strong emphasis on minimizing the release of any isotope for which a feasible recovery technology exists or may be developed. Devices are incorporated into reactor building exhausts to capture particulates and to adsorb gases, thereby preventing escape of radioisotopes through ventilation systems into the environment. The technology has developed to the extent that the radioactivity measured downwind from a nuclear power plant is but a very small fraction of that measured downwind from a coal-fired power plant.

Radioisotopes of iodine are generated continuously within nuclear fuel during normal reactor operation. These isotopes are considered a serious biohazard, but most of them have rather short half-lives. Activated charcoal is an effective medium for adsorbing gases, including elemental iodine and various organo-iodides that may escape into the containment building atmosphere from a ruptured fuel pin. Charcoal's effectiveness is impaired by high humidity, iodine desorption above 250°C, and ignition in air above 300°C. Silver zeolite (AgX) is more effective in capturing iodine species and retaining them above 500°C. The effectiveness of zeolite is not impaired by high humidity nor is it combustible.¹⁻⁴ Major disadvantages of AgX are: high silver cost, susceptibility to "poisoning" by hydrocarbons, and difficulty in recovering silver values when the zeolite is no longer serviceable.

AgX iodine adsorber systems have been in service in the building exhausts of experimental reactors at the Idaho National Engineering Laboratory (INEL) for more than a decade. Substantial operating and maintenance experience has been accumulated during this period, along with credible economic data. An economic analysis of the Loss of Fluid Test reactor (LOFT) AgX system indicated that even with the high initial cost of the silver, this system is more economical to operate than equivalent charcoal systems.⁵ In addition to the advantages of AgX already mentioned, expensive fire detection and suppression systems are not required, the AgX adsorption units will occupy a

smaller volume due to their higher adsorption efficiency, and AgX will provide many times the service life obtainable from charcoal systems.

To comply with the current LOFT specification, 270 lb of AgX with a minimum silver content of 37.5% is required for each 1000 cfm of building exhaust capacity. The total exhaust capacity for currently operating domestic reactors is about 8 million cfm. If all charcoal systems in all domestic reactors were replaced by AgX adsorber units, 11.8 million tr oz of silver would be required. This quantity represents a substantial capital investment that must be weighed against operating economies. AgX has no affinity for the noble gases, so it is unlikely that charcoal adsorbers will be eliminated entirely from reactor building exhaust systems. Even so, when successful processes for AgX regeneration and silver reclamation are demonstrated on a commercial scale, economies of AgX adsorber units should justify more widespread application.

A review of the literature has disclosed no publication dealing with reclaiming the silver values from unserviceable AgX. Were the zeolite structure intact, one would presume that the sodium-silver exchange phenomenon used to produce the AgX could be reversed to reclaim the silver. In view of the quantities of AgX in service at INEL, the potential for replacement of charcoal systems in commercial facilities, and the high percentage of contained silver, it is imperative to develop a process for efficient recovery of the silver values.

A significant quantity of unserviceable AgX became available, providing an opportunity to experiment with processes for silver recovery. A reverse ion exchange technique was marginally successful, as it recovered about two-thirds of the silver from the AgX and produced a radioactive silver sludge requiring additional treatment. A pyrometallurgical approach was more successful. This report describes the efforts and details the results of the development of this pyrometallurgical approach.

BACKGROUND

The virtues of silver-exchanged zeolite as an adsorbent for gaseous radioiodines were first described in 1968,¹ and the INEL has become a major user. The nature of some of the reactor experiments at the INEL demands a more effective and durable adsorbent than the charcoal adsorbers installed in commercial facilities. The first full-scale AgX adsorber unit was installed in the Power Burst Facility (PBF) in 1973. Later, AgX adsorber units were installed in the Loss of Fluid Test (LOFT) reactor building, in the Nuclear Materials Evaluation Facility (Hot Shop), and in various smaller supporting facilities.

Zeolite Poisoning

A common industrial application for zeolites is as "molecular sieves." The specific pore sizes of the crystals enable purification of gases by permitting passage of small gas molecules while blocking and/or adsorbing others, such as hydrocarbons, that are too large to pass through the pores.⁶ Eventually the zeolite becomes saturated or plugged so that it loses its effectiveness and must be discarded. Hydrocarbon sources in a nuclear facility include gasoline and diesel engines, paint and degreaser fumes, Halon fire extinguishers, etc. In some instances, zeolite efficiency may be regained by thermal desorbing treatments (up to 300°C), depending on the nature of the poison.⁶

The PBF zeolite beds were monitored for adsorption efficiency on a routine basis after installation in early 1973. A gradual but small decline in efficiency (from 99.8 to 98.9%) was noted until 1978, when a marked decline was detected after completion of facility modifications to accommodate a new test series. The efficiency had declined to 79%, well below the "lower criterion" of 93%. An investigation disclosed that the AgX had been "poisoned" by a variety of hydrocarbons released to the building atmosphere during the reconstruction period.^{7,8} Later, the PBF adsorber unit was modified to provide better exposure of exhaust air to the AgX and to enable exhaust air to bypass the AgX bed during standby or at other times when the bed was not needed.

Extensive modifications during 1978 to 1980 to upgrade the "Hot Shop" included installation of a large AgX system and the application of about 600 gal of epoxy paint to the Hot Shop's cavernous interior, in that order. Unfortunately, the cause of the poisoning of the AgX system in the PBF facility was discovered just as the paint in the Hot Shop had dried. Fortunately, the exhaust system containing the AgX was deactivated for incorporation of modifications so that the AgX bed was not subjected to the entire solvent load. Fumes entered the chamber by natural circulation, however, and adsorbent efficiency was reduced from 99+% to about 85%.

The LOFT AgX system avoided the fate of the PBF and Hot Shop systems. Based on recommendations resulting from the PBF experience, administrative controls were instituted to restrict hydrocarbon releases in the containment building and to bypass the building exhaust around the AgX beds during periods when the beds were not needed. As a result of these precautions, the LOFT AgX system exhibited an efficiency of 99.9% just prior to the final LOFT experiment conducted in July of 1985, after nearly seven years of operation.^a

Silver Recovery by Ion Exchange

Approximately 1660 lb (753 kg) of poisoned AgX were removed from the PBF absorber unit. This material contained an estimated 558 lb (253 kg) of silver, which at that time had a market value exceeding \$146,000. Normally, the material would have been shipped to a commercial vendor for recovery of the precious metal values; however, the zeolite was found to be radioactively contaminated. The National Lead Company of Ohio, which reclaims precious metals for the U.S. Government, was not interested in reclaiming silver from radioactive AgX. No other vendor was found that was licensed to receive and process this material, so the options narrowed to: (1) finding a vendor to process the AgX at the INEL to reclaim the silver, or (2) disposing of the AgX as radioactive waste at the Radioactive Waste Management Complex (RWMC).

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a. J. H. McDaniel, private communication, EG&G Idaho, Inc., Idaho Falls, ID, December 1, 1988.

Ionex Research Corporation, of Broomfield, Colorado, supplied the AgX used to replace the poisoned AgX in the PBF adsorber unit. Ionex purchases the sodium form of zeolite (NaX) and converts it to AgX by circulating an AgNO_3 solution through a column of NaX at 90°C until the Na ions are replaced. The sodium-silver exchange is essentially complete (99.9%),⁹ and the Ag ions are distributed through the lattice in a reactive form. Ionex agreed to process the contaminated AgX using reverse ion exchange and to purchase the reclaimed silver, which then could be used by them to produce more AgX. Ionex had found that more than 90% of the silver could be recovered from fresh, unused AgX^a and they planned to employ a similar scheme to recover as much silver as possible from the poisoned AgX. An ion exchange circuit was constructed in the Spring of 1981 in the basement of a deactivated reactor building in the PBF area.

A solution containing NaNO_3 and $(\text{CH}_3)_2\text{CH}\cdot\text{NH}_2$ (isopropylamine) was used to flush the ion exchange columns and replace the ionic silver. Isopropylamine is less effective than ammonia for this purpose, but ammonia can produce silver azide, a violent explosive, while the amine does not. The efficiency of the exchange was diminished by physical deterioration of the zeolite beads, which produced fines that channeled and/or impeded flow through the columns, and by reduction of some of the ionic silver to metallic silver, which could not be exchanged or dissolved. New and used zeolites are compared in Figure 1. Darkening of beads due to reduction of silver is evident.

The solution exiting the columns was collected, pH-adjusted when necessary, and treated with sodium borohydride to reduce the silver in solution. The reduced silver settled to the bottom of the collection vessel as a black sludge. The depleted solution was saved and stored for disposal. The sludge was found to be radioactively contaminated, most likely from carrydown of suspended fines; many volumes of wash water were needed to reduce the activity of the sludge to levels acceptable for shipment from the INEL.

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a. D. W. Porrey, private communication, Ionex Research Corp., Broomfield, CO, November 6, 1984.

Figure 1. Appearance of new (bottom) and used AgX.

The degree of silver recovery was limited by economic factors also. After most of the silver is removed from the AgX in the exchange columns, the remainder of the strippable silver becomes increasingly difficult to recover, eventually requiring inordinate amounts of time and solution to remove minuscule quantities of metal. This time-trouble factor controls the economics of exchanging silver from new AgX also, even if recoveries approaching 100% are theoretically possible. The results of the ion exchange effort are summarized in Table 1.

When silver recovery operations were completed, the vendor shipped 1742 lb (790 kg) of wet sludge to his plant and recovered 385.5 lb (175 kg) of silver. The processing equipment was dismantled, wrapped in plastic, and packed into two waste boxes for disposal at the RWMC. The stripped AgX was double-bagged in packages containing 40 to 60 lb (18 to 27 kg) each and placed into the boxes also, along with absorbent material to contain any leakage of free liquid.

Table 1. Summary of silver recovery by ion exchange

	<u>AgX</u>		<u>Ag Content</u>		
	<u>lb</u>	<u>kg</u>	<u>lb</u>	<u>kg</u>	<u>%</u>
Original AgX wt.	1658.0	752.1	557.1	252.7	33.6
Calc. wt. less 13% H ₂ O	1442.5	654.3	556.8	252.6	38.6 ^a
Calc. Wt. fully dried	1370.3	621.6	556.8	252.6	40.6
<u>Washed Ag Sludge</u>					
1st shipment	1074.9	487.6	220.0	99.7	20.5
2nd shipment	667.0	302.5	165.5	75.0	24.8
Total	1741.9	790.1	385.5	174.8	22.1
<u>Stripped AgX, by Difference</u>					
Wt., fully dried	984.8	446.7	171.3	77.7	17.4
Ag recovery efficiency	385.5/556.8 = 69.23% ^b				

a. By analysis

b. Ionex estimated a 60% recovery of Ag.

The "washed Ag sludge" was an end product of the ion exchange process and consisted of metallic silver reduced from solution and given multiple washings to reduce radioactivity to levels acceptable for off-site shipment. The wet sludge was weighed before shipment and the vendor dried the sludge and recovered 385.5 lb of silver by smelting. This silver weight was subtracted from the "fully dried" weight of the original AgX to estimate the weight of the stripped AgX, and from the original silver content to estimate the silver still remaining in the stripped AgX. The potential for silver losses during processing is high and it is not realistic to expect that 171 lb of silver was available for recovery from the stripped AgX, but no other data were available to provide a basis for a better estimate.

Data for moisture and silver contents were provided by the INEL analytical laboratory. What the laboratory assumed to be a representative sample was dried overnight at 300°C. In Table 1, the "fully dried" figures were calculated based on a 700°C drying treatment and a total water content of

17.4% and a silver content 40.6%, compared with 13% and 38.6% for the lower drying temperature used by the analytical laboratory.

Subsequent treatment of this waste to recover the remaining silver values by smelting was plagued with uncertainties with regard to the actual quantity of AgX to be treated and a general absence of data to enable establishment of a credible materials balance for process accounting. This material was not weighed before the ion exchange treatment, so the effects of variable H₂O content, accumulation of extraneous matter during service, or losses during processing cannot be estimated. Thus, conclusions on process efficiency were based on an unverified original weight.

First Smelting Attempts

That the sludge of reduced silver was too radioactive for the vendor to ship off site was unexpected. At least 3000 gal (11,000 L) of wash water was needed to reduce the radioactivity to acceptable levels, and this water had to be collected and transported to an evaporator. It appeared that melting the sludge with a siliceous flux would be a much cheaper and simpler remedy for the contamination problem, particularly since the identified contaminant, cesium, was assumed to form strong silicates. A 500 g sample of wet, unwashed sludge was obtained for a melting trial.

No suitable furnace was available for this work, so a temporary propane-fired unit was constructed by stacking firebrick to form an enclosure, with a port for inserting a large propane burner, another port for crucible access and observation, and a short chimney to direct combustion products and dust to a filtered building exhaust.

The wet sludge sample weighed 539 g, and after drying for 4 h at 200°C, weighed 189 g. The dried sample was halved, mixed with flux, and charged into two "G"-size fireclay crucibles (400 mL cap.). One sludge sample was mixed with 150 g flux, the other with 50 g flux. The crucibles were placed in the makeshift furnace, heated to 1150 to 1200°C (as determined on the crucible wall by an optical pyrometer; the charge was not visible when melted), and maintained at this temperature for 45 min. The entire crucible contents were

poured into steel molds and allowed to cool. The 94.5 g dried sludge samples produced silver castings of 90 and 91 g. The castings and slags were shipped to the laboratory for radiological analysis where it was determined that the silver was "clean" and that the slag was radioactive. This confirmed the premise that melting the sludge with a suitable flux was a much more effective method for separating radioactive contamination from the silver than was leaching by multiple washings.

ZEOLITE MELTING EXPERIMENTS

Considering the relative ease with which a primitive pyrometallurgical method could produce uncontaminated silver from the radioactively-contaminated sludge, it seemed feasible to extend this method to the direct smelting of AgX. Were this approach successful, silver could be recovered easily and efficiently, the radioactivity would be contained in the slag, and the multiple difficulties associated with reverse ion exchange processing would be avoided.

AgX Composition and Analysis

To produce zeolite in bead form for ease of handling and to assure uniform bed porosity, crystals of NaX are ground to 1.0 to 4.5 μm , blended with a clay binder, agglomerated, dried, and screened. The size fraction specified for the AgX application was 10 to 16 mesh (1.7 to 1.0 mm).

Clay binder constitutes at least 15% of the mix, to assure sufficient strength for the beads to endure normal handling, but not more than 25%, so as not to dilute the adsorptive capacity. NaX intended for conversion to AgX is usually specified to contain not more than 20% binder clay. The binder is a mined clay with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.7:1, and contains about 5% Fe_2O_3 , 10% MgO , and 2% CaO as impurities which are not deleterious and not worth the expense of removal.^a Assuming a 100% exchange of Ag for Na in the beads containing 18% binder clay, the Ag content will be 36.7% instead of the theoretical 44.8%.

The formula given for NaX, $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{ H}_2\text{O}$,¹⁰ may also be expressed as $(\text{Na}_2\text{O})_{43}[(\text{Al}_2\text{O}_3)_{43}(\text{SiO}_2)_{106}] \cdot 276 \text{ H}_2\text{O}$. The latter form, while not indicative of the actual structure, is more representative of the compounds encountered when NaX is melted. An analogous rearranging of the formula may be done for AgX; however Ag_2O is unstable at moderate temperatures and cannot be relied upon to combine with the excess oxygen provided by the AlO_2 .

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a. T. Latham, private communication, Linde Molecular Sieves, Houston, TX, May 31, 1985.

Table 2. Compositions of 13X zeolite

Component	Compositions Calculated According to Given Formula (wt%)				Compositions According to to Analysis (wt%)	
	NaX w H ₂ O	AgX w H ₂ O	AgX 5% H ₂ O	AgX no H ₂ O	New AgX	Stripped AgX
Na ₂ O	14.5	0.0	0.0	0.0	1.27	10.56 ^a
Ag	0.0	36.1	42.5	44.8	41.97	9.80
Al ₂ O ₃	23.8	17.1	20.1	21.2	19.11	26.59
O ₂	--	2.7	3.2	3.3	--	--
SiO ₂	34.6	24.8	29.2	30.7	35.07	49.35
H ₂ O	27.0	19.4	5.0	0.0	--	--
CaO	--	--	--	--	--	1.46
Fe ₂ O ₃	--	--	--	--	1.14	1.70
MgO	--	--	--	--	1.44	0.54

a. If Na were converted to Ag, the total Ag would be 36.9%; if Ag were converted to Na, the total Na₂O would be 14.4%.

Table 2 shows the formula compositions of NaX and AgX expressed in weight percent, with the first two columns showing the shift in weight percentages of components that results from substituting Ag for all of the Na. The next two columns show the percentage shifts that result from removing the water from AgX, while the last two columns show actual AgX analyses.

The (AlO₂)₈₆ is equivalent to (Al₂O₄)₄₃, or (Al₂O₃+½O₂)₄₃. The three columns in Table 2 for the formula composition of AgX show oxygen as a component because of the instability of Ag₂O at the elevated temperature.^a In the case of the stripped AgX, the sample was taken from one of the batches and the value of 9.8% Ag is apparently not representative of the entire lot, as stripping efficiency varied between batches. The level of impurity oxides

a. Ag₂O is stable in air at room temperature. A small amount of decomposition occurs at 100°C and complete decomposition to Ag and O₂ occurs above 300°C.¹¹

in the stripped zeolite is higher than expected from the binder clay. This is attributed to dust and other particulates in the building atmosphere that entered the ventilation system and lodged in the zeolite bed.

The quantity of refractory compound to be converted is determined by subtracting the weights of the bound water and the contained silver from the weight of the AgX to be treated. Water was driven off by heating the sample for at least 1 h at 700°C or higher, while the silver content was determined by smelting an AgX sample as would be done in a crucible assay. Unless the AgX has been processed to remove some of the silver or it is contaminated with considerable extraneous matter, the manufacturer's assay report may be used in lieu of a smelting assay. If an assay report is not available, a value of 38% silver may be assigned arbitrarily to the dry weight of the AgX. If the silver is to be salvaged from such a small quantity of AgX that the cost of refractory analysis is not justified, the material remaining after water and silver are removed may be assumed to be 65% SiO₂ and 35% Al₂O₃.

The radioactive contamination in the batch of AgX stripped by ion exchange was not well characterized nor was the distribution of radioisotopes followed during processing. Analytical emphasis focused on gross radioactivity in order to assure compliance with processing requirements and/or off-site shipping regulations. The meager data on radioisotope content were gleaned from contract correspondence relating to salvaging the silver by ion exchange. The cost of detailed radioisotope analyses for the AgX smelting work was prohibitive even though the information would have been useful in this study.

The results of the radioisotope analyses on the lot of AgX before processing by ion exchange are given in Table 3. These data indicate that ¹³⁷Cs constitutes 98% of the activity in the AgX. The specific activity of ¹³⁷Cs is given as 1.02 x 10⁻² Ci/g;¹² so, if the sample taken was representative of the entire lot, the 753 kg of AgX contained 1.1 x 10⁻⁴ g of ¹³⁷Cs, which corresponds to a concentration of 0.15 ppb. This quantity is below the detection limit for conventional chemical analytical techniques.

Table 3. Unstable isotopes in AgX and in slag
(content expressed in total curies)

<u>In 753 kg of AgX</u>		<u>In 5.9 kg of Slag</u>	
<u>Isotope</u>	<u>Curies</u>	<u>Isotope</u>	<u>Curies</u>
^{57}Co	2.1×10^{-7}	^{154}Eu	5.5×10^{-9}
^{60}Co	4.6×10^{-6}	^{125}Sb	1.3×10^{-8}
^{134}Cs	2.2×10^{-4}	^{134}Cs	2.7×10^{-8}
^{137}Cs	1.1×10^{-2}	^{40}K	3.9×10^{-8}
		^{60}Co	1.6×10^{-7}
		^{144}Ce	2.2×10^{-7}
		^{137}Cs	1.7×10^{-6}

The end product of the ion exchange process was a metallic silver sludge. After multiple washings reduced the activity of the sludge to levels acceptable for off-site processing, it was shipped to Ionex's facility where it was melted under a slag and converted into shot. The silver shot showed no activity. The slag analyses are given in Table 3. The variety of radioisotopes in the slag was unexpected. It appears that the ion exchange process used for silver recovery is selective for certain other elements as well. Because of the limited data, one is reluctant to draw conclusions, as no assurance of representative sampling exists, nor are data available on the wash water of the stripped zeolite that would enable an attempt at a materials balance. Future work should include such studies as they are important from a waste management standpoint.

Flux-Slag Development

The stripped zeolite would produce a radioactive slag requiring disposal at the RWMC. Disposal space at this facility is limited, it was important to minimize the quantity of flux used and not increase the volume of the slag unnecessarily. Other benefits accruing from a minimum flux addition are more silver-containing material per charge (or fewer charges) and lower energy consumption per unit quantity of silver recovered. Use of the minimum flux addition was also supposed to produce the usual desirable slag

characteristics, namely: (1) low melting point to reduce energy consumption (and in this case to reduce escape of volatile cesium), (2) high fluidity in the temperature range of interest (1000 to 1300°C) to aid the escape of evolved gases and to facilitate agglomeration and settling of silver droplets, (3) a minimal tendency to attack the crucible, (4) a very limited tendency to leach after disposal, and (5) low cost.

The $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio in AgX is similar to that encountered in many industrial refractories, thus it was obvious at the outset that common ceramic crucibles would not endure a flux that was appropriate for zeolite. The task was equivalent to formulating a flux which would render a "2600" insulating firebrick into a non-viscous liquid at 1200°C.

A flux is added to refractory oxides in order to form a new composition with a lower melting point that is readily fusible in the temperature range used by the process of interest. Soda ash (Na_2CO_3) is an inexpensive, indispensable source of Na_2O that, in combination with litharge, borax, and other metal oxides, has been used for centuries by assayers to make siliceous ores tractable in their furnaces.

The three-dimensional network formed by silica tetrahedra persists without dissociation at temperatures well beyond the melting point so that silica-rich melts are inherently viscous. When a metal oxide such as Na_2O is added to a silica melt, an excess of oxygen ions is introduced which interrupts the bridging necessary to maintain bonding between the SiO_2 tetrahedra. The double oxygen bond that constituted the shared corner of two tetrahedra becomes a single oxygen bond so that the tetrahedra corners are no longer joined.

Slags are characterized as acid or basic according to the "silicate degree," depending on the slag's tendency to react with the containing refractories, and perhaps more important, depending on the slag's ability to refine the underlying metal by selectively removing impurities.

Applicability of Phase Diagrams

The $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ ternary phase diagram is shown in Figure 2 with the $\text{SiO}_2-\text{Al}_2\text{O}_3$ binary phase diagram attached to the appropriate side. The ternary shows a liquidus surface with isothermal liquidus contours at 100°C intervals. The range of $\text{SiO}_2-\text{Al}_2\text{O}_3$ compositions that qualify as "fireclay" are indicated on the binary, as is the range of compositions for AgX used in this study.

Figure 2. Ternary phase diagram of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ with $\text{SiO}_2-\text{Al}_2\text{O}_3$ binary attached. Adapted from Reference 13, Figures 314 and 501.

The composition of stripped AgX and the theoretical compositions of NaX and AgX are located as well. By drawing lines across the ternary from "AgX Range" to the Na₂O corner (dotted lines, Figure 2), one can estimate the effect on the liquidus of adding only Na₂O. The lowest melting region on the ternary that is intersected by this traverse is reached at about 38% Na₂O.

The lowest liquidus temperature shown on the ternary is 732°C, and it is obtained by using a composition of 26% Na₂O, 62% SiO₂, and 12% Al₂O₃, or SiO₂/Na₂O = 2.5, or (SiO₂ + Al₂O₃)/Na₂O = 2.7. Converting AgX to this composition requires dilution of Al₂O₃ with SiO₂ and Na₂O. An experimental melt using this mix produced a stringy and viscous slag as expected, and confirmed that low melting point and high fluidity are not necessarily related. If a minimum slag volume is a major objective, adding SiO₂ is counterproductive. Subsequent experimentation generally followed the path delineated by the traverse to the Na₂O corner of the ternary. These efforts are described in "Preliminary Experimental Slags".

Certain metal oxide combinations are more effective than Na₂O alone with respect to improving fluidity. Other compounds that promote fluidity and have a solvent action on aluminosilicates are: B₂O₃ (boric oxide), Na₂B₄O₇ (borax glass), Na₃AlF₆ (cryolite), NaF (villiaumite), and CaF₂ (fluorite). Boric oxide and borax glass are considered, along with SiO₂, as acids. Both have much lower melting points than SiO₂ (577 and 743°C, respectively, compared to 1723°C for SiO₂) and increase fluidity of silicate melts to some extent. The SiO₂-B₂O₃ binary shows a eutectic at less than 500°C, and the Al₂O₃-B₂O₃ binary has a eutectic at 1035°C, but more than 90% B₂O₃ is required to achieve the eutectic composition in both cases.¹³ The fluidizing effect on silicate melts may be attributed to a tendency of B₂O₃ to form triangular BO₃ units. The formation of sheet or ribbon structures among the SiO₂ tetrahedra would increase fluidity.

Of the fluorides, Na₃AlF₆ is considered the best solvent for alumina, but CaF₂ is cited most often as a fluidizer for high-alumina silicate slags, with CaF₂ additions equal to 60 to 100% of the alumina content.¹⁴ Binary phase diagrams for the candidate fluorides show eutectics as low as 950°C and most ternaries with a fluoride component appear more promising than their related

binaries.¹³ As was the case with B_2O_3 , the fluoride compounds must comprise 90% or more of the mix to achieve the eutectic composition. Fluidity suffers if suspended crystalline solids exceed 50%.¹⁵

The fluoride ion is more electronegative than the oxide ion and will displace oxygen from the SiO_2 tetrahedra. Also, it decreases viscosity by disrupting the interaction between metal and silicate ions so that it serves both as a flux for silica and a fluidizer for molten silicates.¹⁶

Phase diagrams offered some clues as to possible flux compositions but provided no direct answers to vexing questions regarding the conversion of an aluminosilicate to a low-melting, low viscosity liquid. Considering the variety of candidate flux components and the constraints imposed by processing requirements, it became apparent that the complexity of the slag would exceed the capability of the diagrams to materially assist in the formulation of a flux. An empirical approach was the obvious alternative. This approach was pursued.

Crucibles

Fireclay assay crucibles were used for preliminary slag studies because they were abundant and because the time of contact with slags at elevated temperatures was expected to be short (30 to 45 min). Unfortunately, in some cases enough of the crucible would dissolve to mask the effect of the flux. Clay-graphite crucibles were an improvement in this respect, but aggressive slags dissolved the clay binder. The fireclay crucibles were usually limited to a single melt, while the clay-graphite vessels would endure 4 to 6 heats before they became so thin that using them for additional melts appeared risky.

The most durable crucibles were of carbon-bonded silicon carbide. Vessels of this composition obtained for experimental work were cylindrical, with internal dimensions of $2\frac{3}{4}$ in. in diameter by $5\frac{1}{4}$ in. high, with a $\frac{3}{16}$ -in. wall thickness (70 x 145, 9.5 mm). The total capacity was 200 mL and the working volume was 140 to 150 mL. These crucibles were coated with a siliceous glaze to retard oxidation, which was troublesome occasionally as it

tended to drain off hot crucibles and glue them to the furnace hearth. Also, it was necessary to melt a wash slag in a new crucible to remove this glaze from the interior before conducting fluidity tests. These crucibles usually would survive at least 10 heats and were certainly more suitable and cost-effective than fireclay or clay-graphite crucibles.

Although carbon-bonded silicon carbide was most resistant to direct attack from the slag, it presented a reducing environment to the melt. Reactions were possible that would not be encountered in ceramic vessels and that precluded the use of some fluxing agents. For example, PbO would be reduced to lead at the expense of the carbon bonding and would alloy with the silver.

Methods of Determining Fluidity

Charged crucibles were placed in a propane-fired furnace and heated to 1200 to 1250°C. Slag temperature was monitored with an optical pyrometer and checked occasionally with a dip thermocouple. The pyrometer and thermocouple readings agreed within 10 to 30°C. Thermocouple use was minimized, as some slags dissolved the alumina sheath.

Relative fluidity was determined by pouring into a steel trough, by pouring onto a horizontal steel plate and comparing pancake diameters, or by pouring onto an inclined steel plate and comparing the lengths of the runs. None of these methods was completely satisfactory, particularly when compared to the quantitative data that may be obtained from a viscometer, yet they enabled quick elimination from consideration those compositions that were obviously unsatisfactory.

Experiments using the trough and the horizontal steel plate involved too much subjectivity. Small differences in temperature impaired judgement, and differences in charge weight affected pancake size. The pancakes shattered on cooling, and while the pieces could be assembled to enable a diameter measurement, loss of fragments prevented establishment of a weight-to-diameter relationship. The $\frac{1}{4}$ -in. (9.5 mm) inclined steel plate produced the most definitive fluidity results. It was placed at a 30-degree angle, as some

samples would slide off during the pour when the plate was inclined at 45 degrees.

Preliminary Experimental Slags

The quantity of new AgX available for melting studies was not large enough for an extensive examination of slag compositions if such was needed in order to discover the most suitable flux mix. Since fluxing $\text{SiO}_2\text{-Al}_2\text{O}_3$ was the issue, silica sand and alumina cement (99+% Al_2O_3) were blended in the proportions needed to simulate the composition of zeolite, along with additional ingredients to duplicate the impurity content and to produce the candidate fluxes.

A variety of preliminary slag compositions were tried on the inclined pour plate, and it soon became evident that CO_2 evolution from decomposition of soda ash and other carbonates was a major problem. Many melts could be brought to pouring temperature very slowly, particularly in the 800 to 1000°C range, so that foaming did not cause crucible overflow. Some of these melts required more than 3 h to reach pouring temperature. Translated into 100 lb (45 kg) production-sized heats, one or more days would be required to reach pouring temperature. In addition, CO_2 evolved from the melt attacked both clay-graphite and the carbon-bonded silicon carbide crucibles according to the reaction: $\text{O}_2 + 2\text{C} \rightarrow 2\text{CO}$. The CO ignited as soon as it contacted the atmosphere, so that the slag surface was spotted with small puffs of yellow flame.

An alternative to Na_2CO_3 was needed, as Na_2O was a critical part of the flux. The alternative must be readily available and inexpensive. Sodium hydroxide seemed an obvious choice but no data could be found in the literature or elsewhere to indicate whether dry NaOH could be used in this manner. Na_2CO_3 begins to decompose prior to reaching its 852°C melting point, but NaOH melts at 318°C and it may be heated to boiling (1390°C) without decomposition. It was suspected that in the presence of silica, a $x\text{SiO}_2 \cdot y\text{Na}_2\text{O}$ could be formed in the temperature range of the process. Whether an aluminosilicate could be decomposed might be another problem. Arbitrarily selecting the reaction, $2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$, the ΔG was determined and

it appeared that the reaction tended to occur even at room temperature. A trial charge made by mixing NaOH pellets with silica flour in the molar proportions of the above equation was melted in a silicon carbide crucible. A homogeneous, moderately fluid pour was made at 1200°C. No foaming was noticed during heating and less than an hour was required between starting and pouring.

The next concern was whether molten NaOH could pluck SiO_2 from the aluminosilicate structure of the zeolite. Mixing silica sand with alumina cement does not duplicate the zeolite network. A 50 g charge of AgX was mixed with NaOH and CaO and heated to 1300°C. A rather viscous slag resulted which cooled to a clear amber glass, and a 16.15 g silver button was recovered. Substitution of NaOH for Na_2CO_3 not only solved the foaming problem but provided an opportunity to reduce the escape of volatile cesium by producing a liquid more than 500°C below the melting temperature of Na_2CO_3 , restricting direct exposure of cesium to air until it could react with silica.

Boria is more similar to silica than is alumina with regard to its affinity for metal oxides. Since fluorides were to be added as a function of the alumina content, the fluoride present will be expressed as the alumina-metal fluoride ratio. These notations seem more appropriate and convenient for the purposes of this work, but there is no intent to ignore possibilities that boria may improve fluidity in melts containing alumina and that fluorides may improve the fluidity of silicate melts.

Small quantities of reagent grade Na_3AlF_6 , NaF, and CaF_2 were available for experiments to determine the amounts of these compounds needed to achieve the desired melt fluidity and reduce the need for large amounts of metal oxides. Maintaining the $(\text{SiO}_2 + \text{B}_2\text{O}_3)/\text{MO}$ ratio at about 1.0, increasing amounts of Na_3AlF_6 produced noticeable viscosity reductions but the cryolite supply was exhausted before experimentation was completed. An $\text{Al}_2\text{O}_3/\text{Na}_3\text{AlF}_6$ of 3.9 produced the best results. This ratio corresponds to a cryolite addition equal to about half the calculated alumina weight. With a $(\text{SiO}_2 + \text{B}_2\text{O}_3)/\text{MO}$ of 1.5, both CaF_2 and NaF produced adequate fluidity when $\text{Al}_2\text{O}_3/\text{CaF}_2 = 1.0$ to 1.5, or $\text{Al}_2\text{O}_3/\text{NaF} = 0.5$ to 0.7.

Final Experimental Slags

Based on the experience obtained to this point, a series of slags was formulated for testing in a more quantitative manner using the inclined plate. The composition of stripped AgX given in Table 2 was used as the basis for a "dummy" zeolite mix that also included the impurity oxides. Variable quantities of Na_2O (as NaOH), B_2O_3 (as $\text{Na}_2\text{B}_4\text{O}_7$), and NaF were added as fluxes to produce the compositions given in Table 4. The Na_2O and B_2O_3 in the borax glass are listed separately and the Na_2O shown includes that from NaOH plus that derived from borax glass.

Enough mix to produce a 300 g melt was loaded into the silicon-carbide crucibles, and crucibles containing the first three mixes were loaded into the furnace and heated to 1220°C . Flux suitability was determined by the run lengths given at the bottom of Table 4. To develop the value for MO used for the ratio, the impurity oxide content was added to Na_2O on a molar basis. Mixes 4 and 5 were formulated based on the results of the first three melts.

Table 4. Experimental slag compositions [wt % and mole % (m/o)]

Mix → Component ↓	#1		#2		#3		#4		#5	
	wt%	m/o	wt%	m/o	wt%	m/o	wt%	m/o	wt%	m/o
SiO_2	37.1	38.2	36.9	39.2	37.4	40.9	33.9	35.9	32.1	33.1
Al_2O_3	20.0	12.1	19.9	12.5	20.2	13.0	18.3	11.4	17.3	10.5
B_2O_3	5.7	5.0	11.3	10.3	11.4	10.8	10.8	9.9	10.3	9.2
Na_2O	17.5	17.4	17.9	18.5	22.6	23.9	23.6	24.2	22.4	22.4
CaO	1.1	1.2	1.1	1.2	1.1	1.3	1.0	1.2	0.9	1.1
MgO	0.4	0.6	0.4	0.6	0.4	0.7	0.4	0.6	0.4	0.5
Fe_2O_3	1.3	0.5	1.3	0.5	1.3	0.5	1.2	0.5	1.1	0.4
NaF	17.0	25.0	11.3	17.1	5.7	8.9	10.8	16.4	15.4	22.7
SiO_2/MO	1.9		1.9		1.5		1.4		1.4	
$\text{SiO}_2+\text{B}_2\text{O}_3/\text{MO}$	2.2		2.4		2.0		1.7		1.7	
$\text{Al}_2\text{O}_3/\text{NaF}$	0.48		0.73		1.46		0.70		0.46	
Run Length (in.)	10.5		13.5		14.0		21.5		35.0	

From the data in Table 4, it appeared that increases in Na_2O and NaF produced the most substantial fluidity improvement. Based on this observation, additional experiments were performed using the new AgX saved for this purpose. These melts were poured into a trough rather than on the inclined plate in order to collect the silver and because the slags had become so fluid that they would run beyond the bottom of the inclined plate and pool on the floor, making run length comparisons useless.

Increasing CaO and NaF enabled a reduction of B_2O_3 . The fluidity was improved compared to that obtained from Mix 5 in Table 4, even though the silica and alumina remained about the same. Adding other metal oxides such as PbO and Fe_2O_3 may have improved fluidity even more, but some oxides are easily reduced by crucible carbon and would have alloyed with the ingot. The mix listed below resulted from the work just described.

<u>Component</u>	<u>wt%</u>	<u>m/o</u>
SiO_2	32.5	34.7
Al_2O_3	17.5	11.1
B_2O_3	5.1	2.3
Na_2O	22.3	23.2
CaO	12.2	14.0
MgO	0.4	0.5
Fe_2O_3	1.1	0.5
NaF	9.0	13.8

$$\begin{aligned} \text{SiO}_2/\text{MO} &= 0.91, & (\text{SiO}_2 + \text{B}_2\text{O}_3)/\text{MO} &= 0.97, \\ \text{Al}_2\text{O}_3/\text{NaF} &= 0.80 \end{aligned}$$

Flux additions were made on the basis of kg of flux per kg of AgX after determining the refractory remaining when water and silver were removed. Therefore, in order to convert the stripped AgX to the composition above, for each kg of AgX, add 0.181 kg of Na_2O (as 0.199 kg of NaOH ; stripped AgX already contains 10.6% Na_2O), 0.087 kg of borax glass, 0.132 kg of CaO , and 0.106 kg of NaF . With this flux addition, each kg of stripped AgX now represents about 1.5 kg of total charge. A volume reduction of 50% occurs when AgX plus flux is converted to slag.

EQUIPMENT, DESIGN AND CONSTRUCTION

General Considerations

Based on the recovery data given in Table 1 for ion exchange processing, about 985 lb (447 kg) of fully dried stripped AgX was available for treatment. The difference between the estimated original silver content (557 lb) and the quantity actually recovered (385.5 lb) indicated that as much as 171 lb of silver still remained in the AgX, or that the silver content was reduced from 38.6 to 17.4% of the fully dried AgX weight. Were flux added on the basis described in the previous section, the total quantity of material to be treated would be 1940 lb if the moisture content of the AgX were assumed to be 13%. The recovery, drying, and weighing of the stripped AgX proved most of these estimates to be correct.

In order to design a smelting capability that would complete the task in a reasonable time, and to obtain experience and generate data applicable to a production-scale operation, it appeared that equipment should be designed to process the AgX in 10 to 15 heats, or that the crucible should have a capacity of between 125 and 200 lb (55 to 90 kg). No equipment was on hand to meet these requirements, or which could have been modified to do so. A 50 kW induction furnace was the preferred heating unit, but no surplus equipment could be found and the scope of the project could not justify the expense of a new unit. A 175-gal propane storage tank had been installed for another project and gas lines were already in place near a large HEPA-filtered^a exhaust hood in an area suitable for conducting the smelting operations. The flux-slag experiments had demonstrated the capability of a propane-fired furnace to achieve temperatures above 1450°C. Disposal of the large volume of hot combustion gases (which would have been avoided by induction melting) could be accommodated by the available exhaust hood. The decision to construct a propane-fired unit was based on the above considerations.

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a. High Efficiency Particulate Air filter, which retains 99.97% of particulates $>0.3 \pm 0.03 \mu\text{m}$.

Smelting Furnace Design, Construction

The most expeditious approach was to construct a furnace from insulating fire brick. To minimize brick cutting, a cubic shape sized to multiples of brick dimensions was employed. Castable refractories would have permitted a weight-saving cylindrical shape and enabled replacement of components if necessary without a total tear down and rebuild. High labor cost for form construction did not seem warranted in view of the anticipated maximum 15 heats, and insulating firebrick was certainly adequate for the service intended. A metal enclosure was needed that was sufficiently rigid to contain the brick and support a loaded crucible during heating and during the load shift that occurs when tilting the furnace to empty the crucible.

The Starrbide™ No. 175 crucible was chosen based on the successful performance of the smaller carbon-bonded silicon carbide crucibles during the flux development studies. This crucible was of the "bilge" design, and was shipped with a separate 12-in. pouring spout. The manufacturer rates this crucible for 587 lb (266 kg) of red brass, which corresponds to an internal volume of 32 L. The external crucible dimensions were given as 19.4 in. high, with a 15½ in. bilge diameter (50 x 40 cm). The design developed from the considerations given is illustrated in Figure 3. The furnace was tilted manually, using a handwheel crank driving a roller chain through a reduction sprocket to a winch. The handwheel was equipped with a spring-loaded brake to permit leaving the furnace in a tilted position with the handwheel unattended. Pressing inward on the crank handle released the brake and enabled rotation. The 0.313 in. (8 mm) steel cables were attached to the winch and passed beneath the furnace to attachments in the extensions at the front of the furnace frame. As the cable was wound on the winch drum, the rear of the furnace was lifted, and when the rear corner passed the level of the winch the load was transferred to the extensions. Continued winding would tilt the furnace until the crucible was empty. The trunnions were placed so that the center of gravity of the furnace was within the support frame at all times. A form was constructed so that a crucible cover could be made from a castable

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™American Refractory and Crucible Co., North Haven, CT.

Figure 3. Isometric drawing of zeolite smelting equipment.

refractory that had better insulating properties but was less durable than the covers offered by the crucible manufacturer. The cylindrical projection on this cover was sized to fit the tongs for the refining crucibles so that the cover could be removed for charging the crucible or for pouring. A layer of kaolin insulating wool was placed on the cover to further reduce heat loss.

Ingot-Slag Mold

Once the smelting operation was completed and the silver had separated from the slag and collected at the bottom of the crucible, it was necessary to empty the crucible and begin smelting the next charge. It was planned to pour the slag and silver together into a receptacle, where the slag and silver would separate again while still liquid, and to remove the solidified slag from the silver ingot when it cooled to room temperature. The pouring receptacle constructed to accomplish this is shown in Figure 3.

The pouring receptacle was of sufficient volume to hold the contents of a full crucible, even though it was not expected that the crucible would ever be filled to the level of the pouring spout entrance. When the furnace was tilted, the slag emptied from the crucible first, while silver was the last liquid to leave. Silver would pour through the still-molten slag in the receptacle and settle into the ingot pocket, displacing the slag from this cavity. On cooling, the difference in contraction coefficients would break the ingot from the slag so that separation would have already occurred when the pouring receptacle was removed from its platform and emptied by inverting and dumping on the floor.

Gas Burner

Two propane burners were arranged to enter the crucible cavity tangentially near the bottom so that the flames did not impinge directly on the crucible wall, and to promote circumferential circulation of the flames.

The burner tubes were fabricated from 1½-in. schedule 40 pipe and sections were joined by "long-radius" weld elbows to minimize flow obstruction. The burner tips were machined from Type 304 stainless steel and

were threaded into seal plates, under each of which was compressed a patch of kaolin wool blanket. A section of kaolin insulating board encircled the exit of the burner tip in the combustion chamber. It would become incandescent very quickly and sustain the flame while the chamber and crucible were heating.

Pressurized air was supplied by an Ametek No. 115750, 2-stage, single-speed vacuum cleaner motor and conveyed to a double eductor assembled into a standard 1½-in. "tee" fitting (see Figure 4). Pressure was regulated by venting air using a ported band around the motor housing, which assured an air flow around the motor windings regardless of air demand. A 0 to 15 oz/in.² pressure gage was tapped into the motor housing.

Propane was supplied at 9.4 oz/in.² to the bottom of the eductor tee and was metered into the reduced pressure region from which it was drawn into the airstream and mixed for combustion. A Pt/Pt-13Rh thermocouple was cemented into the crucible cavity lining and the fuel/air ratios producing the maximum temperatures were recorded. The rear of the furnace, with the blower, burners, and gages is shown in Figure 4.

Refining Furnace

The crude silver ingots produced by the smelting process would have radioactive slag adhering to their surfaces as well as entrained in the shrinkage cavities. Reducible impurities such as Cu, Ni, Pb, etc., would be alloyed with the recovered silver. Also, the crude ingots would not be in a marketable form. Before recovery operations could be considered complete, it was believed to be necessary to remove all traces of radioactive slag and produce a "standard" ingot that was verified by assay to be refined silver.

Silver refining was done by bubbling oxygen through the molten silver to oxidize the metallic impurities, which then floated to the surface where they could dissolve into the slag and then be removed by dipping. As noted earlier, Ag₂O decomposes completely in air above 300°C; thus this compound will not form at 1100°C. However, oxygen will dissolve to a considerable extent in molten silver, particularly at temperatures just above the melting

(a)

(b)

Figure 4. Rear of smelting furnace, showing: (a) blower, air/gas mixer, and gages, (b) cross-section of double eductor.

point. When silver solidifies, the solubility of oxygen decreases suddenly by a factor of 20 (from 0.25 to about 0.013%)¹⁴ so that the ingot surface erupts during solidification. Bubbling oxygen through the melt causes the bath to approach oxygen saturation, so that once the impurities are removed it is necessary to deoxidize the bath before the ingots are poured. It is also necessary to prevent reintroduction of oxygen by exposure to air before the ingots solidify. A number of deoxidizers may have been suitable. Carbon rods were available and were submerged in the melt until CO₂ evolution ceased. A flaming-gas reducing blanket protected the silver ingots from redissolving oxygen before solidification occurred.

Refining Furnace and Accessories

Time and funding constraints mitigated against construction of the small tilting refining furnace envisioned in the original plan. A box furnace was constructed instead to enable application of the refining steps just described. The furnace was sized to contain four No. 8 Starrbide™ crucibles so that four full-sized crude ingots (about 50 kg) could be processed simultaneously. This processing rate was about double that anticipated in the original plan but it would require considerably more manual effort.

The box furnace was constructed of 2600 insulating firebrick surrounded by 1½-in. insulating board, and was mounted in a frame so that it was at a convenient height for manual crucible transfer. A single, 1½-in., blower-powered propane burner penetrated the furnace wall near the access door where the flame would impinge upon the crucible being treated. The burner was angled to the rear to direct the heat toward other crucibles and out the chimney instead of toward the operator. The access door was cantilever-mounted and pivoted so the hot door face could be rotated away from the operator when it was opened. An access port above the door provided a small opening for observation of the melt, introduction of the oxygen lance, addition of flux, removal of slag, insertion of carbon rods, and monitoring of melt temperature. A thermocouple was cemented into the furnace wall adjacent to the burner port to measure furnace temperature and determine fuel/air ratio settings. The completed refining furnace, shown in Figure 5, was placed in

Figure 5. Refining furnace, pouring table, and accessories.

front of the smelting furnace so that the chimney was directed into the exhaust hood.

The ingot molds were fabricated from 11 ga stainless steel. The low mass of these molds, as compared to the cast iron molds normally used in this application, required a water-cooled table to accelerate ingot solidification. Four ingot molds are shown arranged on the mold cooler in Figure 5. The mold cooler consisted of two copper bars with tubing soldered to the underside to enable water to carry away the heat. The copper bars were bolted to a steel frame. Chilling the bottom of the thin ingot molds promoted directional solidification and reduced internal porosity.

A crucible rest was constructed to steady the crucible during pouring of the 100-oz ingots. The loaded crucibles were quite heavy and the operator's insulated gloves became hot when retrieving the crucible from the furnace and from remaining in close proximity to the hot crucible, the ingots, and the flame blanket during pouring. The crucible rest consisted of a cart that rolled on a short section of track and incorporated a fulcrum for resting the crucible tongs and to facilitate rotation of the tongs to enable pouring from the crucible. Rolling the cart on the track enabled moving the crucible from mold to mold without having to lift it. The track was part of the base of the mold cooler assembly. The crucible tongs are shown lying across the crucible rest cart in Figure 5.

The "goosenecks" over each mold (Figure 5) provided the flame blanket to minimize oxygen pickup during pouring and ingot solidification. A perforated tube was substituted for the goosenecks later in the program to provide better flame blanket coverage.

The pouring table consisted of a 32 x 48 in. (81 x 122 cm) steel plate mounted on legs so that the table surface was near the elevation of the furnace floor, but not so high that it interfered with opening the furnace access door. The table surface was framed with angle iron and covered with a steel floor grating to contain the flood of molten silver in the event that a crucible broke, was tipped over, or was dropped during transfer. The grating would cause the spilled silver to solidify into miniature ingots and

facilitate picking up the spill and recharging into a crucible. Fortunately, there was no opportunity to test the effectiveness of the design on a major spill, but the table top did contain the small spills and shot produced during routine casting operations.

The gas and water lines were easily disconnected, which permitted removing the crucible-rest/mold-cooler assembly from the table as a unit. The grating could then be lifted or removed to expose the smooth surface of the steel plate for sweeping. After reassembly, the table top was checked for water spills and the water lines inspected for leaks to avoid the hazard that occurs when water is trapped under hot metal.

A platform built under the pouring table was used for storing crucibles and tools as well as for supporting an ABS tub containing several gallons of 2% H_2SO_4 solution. When the 100-oz ingots had solidified, the molds were removed from the mold cooler and the hot ingots were dumped on the table grating. The ingots were then quenched in the H_2SO_4 solution to clean and brighten the surface. The bottom of the tub was covered with a layer of sand so that hot ingots would not melt through the bottom of the tub before they had cooled. The ingot identity numbers were stamped into the surface as soon as they were retrieved from the tub.

PRODUCTION

Retrieving and Drying Stripped AgX

The two waste boxes containing the AgX stripped by ion exchange were shipped to the melting facility. Under the supervision of a health physicist, the bags of stripped AgX were located among the various items of discarded equipment and packages of miscellaneous contaminated waste. Some bags leaked where they had been punctured or torn and these were placed in a third bag. Retrieved bags of AgX were loaded into three ABS polymer 55-gal drum liners for storage until drying operations could begin.

Most of the bags contained free liquid which was dark grey or black and which appeared to be a suspension of reduced silver and mud from deteriorated zeolite. In order to minimize silver loss, when the bags were opened the free liquid was poured into a filter bucket before the AgX was loaded in the drying trays. Also, the emptied bags were rinsed and the wash water and residues were poured into the filter bucket before the bags were discarded. Eventually, the filters were dried, placed on one of the last drying tray charges, and ashed.

The drying trays were enameled steel pans, 28 x 40 x 9 cm, which would contain 10 to 12 kg of wet AgX. Bed depth was about 15 cm. Unfortunately, the drying oven would accommodate only one tray per drying cycle, so 74 cycles were required to dry the entire batch of wet AgX. The drying oven was set at 275°C and the charges were dried for 4 h during the day and 16 h overnight. The charges were allowed to cool for 2 h before weighing and pouring into storage buckets to avoid melting the poly bag bucket liners. Each bucket contained 18 to 20 kg of dried AgX.

The bags were sealed and the bucket lids snapped on to prevent readsorption of moisture during storage and so the containers could be stacked until needed. The last tray of dried AgX did not fill a bucket. The content of this bucket (8.9 kg) was reserved for smelting studies, as only preliminary slag studies had been done at that point. Equipment design had not begun, for

it was only after the stripped AgX had been dried and weighed was a credible value available for the total quantity to be processed.

The 4 h drying cycle reduced the weight of the wet AgX by 16 to 20%, while samples dried overnight lost 27 to 37% of their weight. Some weight loss variation was attributable to differences in the original moisture content in each drying tray, but it was apparent that a longer drying time had a significant effect on moisture removal. Drying tests indicated that the equilibrium water value for AgX dried at 275°C was 6 to 7%. The 10-g laboratory samples would reach equilibrium quickly, but it was difficult to conduct heat to the center of a 12-kg drying tray charge, as well as for water vapor to diffuse from the bottom to the surface of the charge.

The total weight of the wet AgX (not including the liquid poured into the filter bucket) was 1641 lb (744 kg). Evaporated water and decomposed isopropylamine totaled 389 lb (176 kg), leaving 1252 lb (568 kg) of dried AgX. Subsequent drying experiments at 700 to 800°C, using the material set aside for this purpose, indicated that an additional 19.9% weight reduction could be obtained. If the sample set aside for this work was representative of the entire lot, the fully-dried stripped AgX would have weighed 1003 lb (455 kg). The summary of the ion exchange work (Table 1) shows that 985 lb (447 kg) should have been recovered. The 18-lb discrepancy is within 1.8% of the total and indicated that all bags of stripped AgX had been found. The discussion of Table 1 data describes uncertainties regarding the actual quantities of AgX processed.

Preparing and Mixing Charges

About two years elapsed between drying the stripped AgX and full-scale melting trials. Flux experiments and the design and construction of the furnace were done during this period on a time-available basis. In the meantime, the AgX filter bed in the PBF reactor building exhaust system was modified to a more efficient design and PBF found it necessary to sieve all of their AgX to remove <16-mesh beads. The undersize material was recovered, stored in a steel drum and several buckets, and became available for silver reclaiming at about the time the smelting furnace was ready for trials. The

AgX was contaminated with radioactive debris, and because of the manner in which it was packaged, it seemed prudent to process it before the stripped AgX. Thus, the first production-sized heats used AgX fines that had not been partially stripped of silver by ion exchange.

The lot of AgX fines weighed 408 lb (185 kg) and contained an inordinate amount of dust, so precautions were necessary to avoid spreading radioactivity in the work area. No assay report was available. The 700°C drying procedure determined the water content to be 15.8% and the smelting assay indicated the silver content to be 30.01% (35.7% with the AgX fully dried). This value for silver was lower than expected. On this basis, 122.4 lb (55.5 kg) of silver was contained in the 407.7 lb of AgX.

The CaO purchased for the flux composition described previously had not arrived in time to begin the production melts. This delay resulted from specifying CaO with a maximum of 2% MgO, as CaO ordered as "burned lime" may contain 15% or more MgO. Reagent grade CaO was used for the experimental work and the effect of MgO, if any, had not been investigated.

Due to the temporary unavailability of CaO, an interim flux was formulated which closely resembled Mix 5, Table 4. The refractory content of the AgX fines was not analyzed to establish the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio or to determine the impurity content. The refractory composition was assumed to be the same as for stripped AgX (Table 2), but without the Na_2O . On this basis, the nominal slag composition expected to result from adding the interim flux was:

<u>Component</u>	<u>wt%</u>	<u>m/o</u>
SiO_2	33.6	35.1
Al_2O_3	18.0	11.1
B_2O_3	10.0	9.0
Na_2O	18.0	18.2
K_2O	2.0	1.3
CaO	1.4	1.6
MgO	0.5	0.8
Fe_2O_3	1.5	0.6
NaF	15.0	22.4

$$\text{SiO}_2/\text{MO} = 1.6 \quad (\text{SiO}_2 + \text{B}_2\text{O}_3)/\text{MO} = 2.0 \quad \text{Al}_2\text{O}_3/\text{NaF} = 0.50$$

The flux was blended with the AgX in two batches. In the first batch, 227.4 lb (103.1 kg) of AgX was weighed into the mixing drum and 104.2 lb (47.3 kg) of flux was added. In the second batch, 175.7 lb (79.7 kg) of AgX was used and 79.4 lb (36.0 kg) flux was added. The flux ingredients were added on a "g per kg AgX" basis as described on page 22. The mixing drum was rotated for about 2 h. After mixing was completed the drum was allowed to stand for an hour or so to allow the contents to cool so that a spurt of dusty air did not escape and blow contaminated dust into the room when the drum lid was loosened. Thoroughness of mixing was ascertained by the uniformity of color of the mix when weighing out the drum contents into the charge buckets. The AgX was dark gray while the flux components were white, so layering would be unmistakable.

When the desired crucible charge was known, this quantity was divided evenly among 3 or 4 buckets. The heat number and bucket weight were affixed and the lid snapped on to avoid moisture pickup while awaiting charging into the crucible.

Smelting Operations

Furnace Break-in

Since the furnace had not been warmed previously, the burners were fired intermittently in the empty crucible cavity for about 30 min to raise the temperature slowly to minimize thermal stresses and to avoid driving out moisture too rapidly. The crucible was installed and warmed by furnace heat before intermittent burner firing began again. During this operation, the cement holding the crucible spout failed, allowing the spout to droop into its recess. The crucible was removed, cooled, and all of the factory cement was cleaned away from the joint. The spout was re-attached with Jade Set Super™. This compound made a superlative joint and was employed for other crucibles. Once fired, the joint was strong enough to permit the spout to be used as a carrying handle for the crucible.

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The crucible was re-installed and heating continued until the crucible reached 1000°C. The first heat-up provided an opportunity to experiment with fuel/air ratios. A Pt/Pt-13Rh thermocouple was inserted through the rear wall of the furnace and cemented into the lining so that the junction measured the temperature of the crucible cavity surface at about half way from the bottom. The fuel/air pressure ratios that produced the highest wall temperatures were recorded for future work.

The interior crucible wall surface and melt surface temperatures were measured by a Leeds and Northrup optical pyrometer. The interior crucible wall temperature was usually 100 to 200°C lower than the furnace lining temperature. The pyrometer would read within 20°C of a calibrated thermocouple dipped into the melt, depending on the amount of fuming above the melt surface. The slag would attack the alumina sheath protecting the thermocouple, precluding prolonged use, so the optical pyrometer was used most frequently to determine pouring temperature.

Smelting of AgX Fines

Two charge buckets containing 86 lb (39 kg) were set aside for the initial melt. The contents of the first bucket was poured into the crucible when it had reached 900°C after two hours of heating. This charge melted completely within an hour, so the second bucket was emptied into the crucible and the cold mix was stirred into the melt below to hasten healing. Foaming became excessive after 30 more minutes of heating and threatened to overflow the crucible, so the burners were shut off and the melt was allowed to cool until the foaming subsided. Foaming continued after the burners were reignited, but it gradually subsided and had nearly ceased by the time the melt had reached 1100°C. The melt was heated until it reached 1200°C, at which time the burners were shut off and the melt was allowed to cool to about 1150°C. The cooling step was done on the assumption that remaining small silver globules would settle to the bottom more easily if they did not have to compete with rising gas bubbles.

The ingot-slag mold was placed on the floor beneath the pouring spout. At the beginning of the pour, the slag stream would enter the ingot pocket by

virtue of its trajectory. Near the end of the pour, the pouring spout had become nearly vertical and the silver would strike the incline of the mold, even when the mold was shoved against the furnace frame. The distance the slag and silver would fall seemed excessive. The slag tended to splash when it struck the mold and the impact of the silver stream on the side of the mold at the end of the pour would cause shotting and entrainment of the shot in the slag where it had become viscous as a result of chilling against the cold mold wall. Also, because the furnace frame restricted how the mold was placed, the furnace could not be tilted beyond the horizontal in order to completely empty the bilge crucible, as this would cause the pouring spout to swing behind the ingot-slag mold and slag and silver would pour onto the furnace base.

Modifications

An experimental correction of these problems involved elevating the mold by placing it on a steel plate on a stack of bricks so that the top of the mold was about 1 in. (2.5 cm) below the pouring spout. When pouring, the furnace was partially tilted so that the extensions were moved to the rear 9 to 12 in. (25 to 30 cm). The pouring receptacle was then shoved toward the furnace so that the ingot pocket would be directly under the spout when the furnace was fully tilted. Elevating and locating the receptacle in this manner greatly improved the pouring operation. As the furnace was returned to its normal position, it would push the receptacle gently out of the way, sliding it on the steel plate.

When the furnace was tilted more than 90 degree to completely empty the bilge crucible, the pouring spout would swing beyond the vertical, as mentioned. While shoving the mold under the spout would prevent pouring the last of the melt onto the furnace base, silver now would fall from the spout notch in the crucible wall without traveling the length of the spout. This condition would cause some shotting of the stream. The spout angle could not be changed because the Jade Set Super™ could not be removed without breaking the crucible, so the problem was tolerated until the next crucible was installed.

Modifications were made after the fourth melt of AgX fines to place the receptacle on an elevated platform that was welded to a cart equipped with

wheels to roll on a short section of track. The receptacle was now high enough to cause the spout tip to be submerged in the slag when the mold was completely filled. Pins were attached to the cart platform which fitted into the hollow receptacle legs to assure alignment and to prevent sliding off the platform. The receptacle was attached to the front of the furnace body with a link so that the act of tilting the furnace pulled the receptacle and cart assembly into the desired position to enable the silver to pour into the center of the hot slag, directly over the ingot pocket. Even with the pouring spout at a less-than-desirable angle, the silver that fell directly from the crucible wall notch would enter near the center of the receptacle, where the slag was the hottest, and settle into the ingot pocket. Less shot was entrained in the slag after these changes were made. A removable pin attached the link to the receptacle to permit it to be disconnected from the furnace frame and rolled out of the way. This feature facilitated cooling and reduced interference with charging operations for the next melt.

The modifications and additions just described were incorporated into the equipment illustrated in Figure 3. Figure 6 shows the partially-tilted furnace pouring slag. The receptacle was pulled along the track by the furnace as it was rotated, although the furnace-receptacle link is not visible in Figure 6. Also, the crucible spout had been installed at the preferred 15-degree angle instead of horizontally as in Figure 3. The insulated crucible cover was removed just before pouring and is located at the bottom of Figure 6 with the tongs still attached.

Smelting operations resumed when the above-described modifications were completed. Performance was greatly improved and no additional changes were made to the smelting equipment for the remainder of the project.

When the contents of the pouring receptacle had cooled sufficiently, it was lifted from the platform pins and up-ended into a shallow container. If the slag was not radioactive it could be dumped on the floor, as it was in Figure 7. A carbon-black mold release applied by an acetylene torch was sometimes not sufficient for the ingot pocket, so Mold-Cote™ was applied to

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Figure 6. Partially tilted smelting furnace pouring slag.

Figure 7. Cooled crude ingot broken from slag.

the entire mold interior with a brush. The ingots often fell freely from the ingot pocket when Mold-Cote™ was applied. The molten silver would displace the slag from the ingot pocket. The difference in contraction coefficients would break the ingot from the slag on cooling and the only slag remaining with the ingot was that trapped in the shrinkage cavity. Any slag on the ingot could be removed easily with a few hammer taps. The ingot surface was brushed clean, the weight and heat number were stamped into the surface, and it was stored in the vault to await refining.

The slag was broken up so that it would easily fit into a container, be weighed, and set aside for disposal. Slag fragments containing visible silver shot were placed in a separate container and charged into another melt. In Figure 7, the mold platform is near the end of the track and the mold leg-locating pins are visible, as is the mold link on the front of the furnace. The rows of brick at the left and bottom of Figure 7 were placed to contain a major spill in the event the pouring receptacle was tipped over while the contents were molten.

Recovery of silver from the AgX fines was completed in six heats, which required 10 working days, including down time to make the described modifications. A charge of 39 kg was used for the first heat and 48.5 kg for the remaining five heats. A total of 56.2 kg of crude silver was recovered, including 0.55 kg from the smelting assays. Only the slag composition that would be expected to result from adding the flux to the refractory is listed in Table 5. The cost of analyzing the radioactive slag to determine the actual composition was prohibitive, but analyses were obtained later on nonradioactive slags from uncontaminated AgX. Data from the refining process showed that conversion of crude ingots to refined silver was 99.1%, so that 55.7 kg of refined silver was reclaimed from the AgX fines. This amount was slightly more than expected. The data from processing the AgX fines are summarized in Table 5. The results obtained were close to the estimates provided by the smelting assays.

Table 5. Summary, smelting of AgX fines (all weights in kg)

<u>Fines</u>				
Total AgX				182.82
Less 15.8% H ₂ O				-28.88
Less 30.01% Ag				<u>-54.86</u>
Refractory to be fluxed				99.08
<u>Flux</u>				
NaOH	28.40	=	Na ₂ O 22.01 + H ₂ O 6.39	
K ₂ CO ₃	4.17	=	K ₂ O 2.84 + CO ₂ 1.33	
Na ₂ B ₄ O ₇	24.85	=	Na ₂ O 7.65 + B ₂ O ₃ 17.20	
NaF	<u>25.88</u>	=	NaF 25.88	
Totals	83.30	=	(solids 75.58 + volatiles 7.72)	
<u>Expected Slag Composition (%)</u>				
SiO ₂	35.1	Na ₂ O	17.0	MgO 0.4
Al ₂ O ₃	19.0	K ₂ O	1.6	Fe ₂ O ₃ 1.2
B ₂ O ₃	9.9	CaO	1.1	NaF 14.8
<u>Smelting Results</u>				
<u>Heat</u>	<u>Charge</u>	<u>Total Pour</u>	<u>Ingot</u>	<u>Slag</u>
1	38.979	31.720	6.316	25.404
2	48.732	40.590	9.620	30.970
3	48.732	41.463	10.182	31.281
4	48.732	43.587	12.356	31.231
5	48.732	41.195	9.795	31.400
6	<u>31.878</u>	<u>27.332</u>	<u>7.371</u>	<u>19.961</u>
Totals	265.785	225.887	55.640	170.247
Smelting assay Ag <u>0.549</u>				
Total crude Ag recovered 56.189				
<u>Expected Materials Balance</u>				
AgX fines 182.82 + flux 83.30 = 266.12				
Slag 174.66 + silver 54.86 + volatiles 36.60 = 266.12				

Smelting of Stripped AgX

Smelting of silver from the stripped AgX immediately followed smelting of the fines. A visual inspection of the crucible interior for wear and tear indicated that while the first six heats had taken their toll on the crucible wall thickness, sufficient wall remained to permit smelting several more heats. Use of the alternative flux mix was continued because the CaO still had not arrived. Weighing and blending of stripped AgX and flux was done as described on page 36.

The stripped AgX contained only 9.8% silver compared to 30% contained in the AgX fines, so larger charges were used for each heat in order to produce the maximum obtainable ingot. Four charge buckets were used per heat, each of which contained 17 kg of mix. Each crucible charge was 68 kg, compared to the 48.5 kg used for each heat when smelting the AgX fines. Very little "free-board" was available at the top of the crucible when charging was nearly completed, and the temperature was increased very carefully because the crucible would overflow quickly if foaming began. While all of the 68 kg could be added, it became a tedious procedure and consumed an entire shift. The heat was usually ready to pour near the end of the day. After a pour was completed, a bucket and a half for the next melt was added immediately, the cover was placed on the crucible, and the top of the furnace was covered with an alumina wool blanket to conserve heat. This charge was partially degassed and liquified overnight so that startup could proceed more quickly the next morning. Even with careful heating and charging, the time to smelt these heavy charges was such that the pour occurred a little later each day. The last of Mix 2 was used for Heat 10, and the K_2CO_3 was replaced by reagent grade CaO for Mixes 3, 4, and 5 to reduce foaming.

The crucible was replaced after Heat 10 because the side wall had become so thin that it was risky to continue its use. The furnace interior was inspected before the new crucible was installed and small chips and cracks in the lining were patched. The spout for this crucible was elevated 15 degree, as shown in Figure 6. New kaolin wool was packed in about two-thirds of the annulus area at the top of the crucible. This practice was found to reduce heat loss, promote more uniform heating of the crucible, and direct more of

the hot exhaust gases under the pouring spout. Less slag and silver solidified in a hot pouring spout. The new crucible had a slightly smaller volume than the one used previously because it had not yet suffered wall attrition, so adding the large charges was even more difficult. The expected slag composition with reagent grade CaO replacing K_2CO_3 for Mixes 3, 4, and 5 is shown in Table 6.

Replacing the carbonate reduced the foaming problem somewhat, but fine CaO dust would enter the exhaust system and plug the HEPA filter. Up to this time, the HEPA filter would last for at least six melts before the increased pressure differential indicated that it needed to be changed. With CaO in the flux the filter needed changing after two melts. A fiberglass prefilter installed in the exhaust hood extended HEPA changeouts to 4 or 5 melts.

Mixes 3, 4, and 5 were used for Heats 11 through 17. As may be seen in Table 6, less than the intended charge was used for several heats because charging and melting took too much time for some melts to be poured during the normal shift. Heats 15 and 16 were completed using the 68-kg charges by working overtime the previous evening so that more charge could be outgassed and ready for melting the next day.

The technical grade CaO finally arrived and was used in Mix 6, which was the mix originally intended (p. 22). The fluidity of the slag at lower temperatures was improved considerably so that H_2O vapor could escape more easily and reduce foaming. This mix was used to finish Heat 17 and for Heats 18 and 19. Note the size of the charge used for Heat 18.

The slag containing visible silver shot was recovered and recharged, as was done when melting the AgX fines. The practice of recharging this material was discontinued after Heat 11 because heating times were already too long without adding more cold material. Silver-rich slag from Heats 12 through 19 was saved until smelting was concluded and was remelted as a separate heat (No. 20). The ~1 kg of silver recovered from this heat represented 2.6% of the silver recovered from these 8 heats.

Table 6. Summary, smelting of stripped AgX (all weights in kg)

Stripped AgX

Total AgX	567.84
Less 19.9% H ₂ O	-113.00
Less 9.8% Ag	-55.65
Refractory to be fluxed	399.19
(Refractory composition, Table 2)	

<u>Flux</u>	<u>Mixes 1 & 2</u>	<u>Mixes 3, 4 & 5</u>	<u>Mix 6</u>	<u>Total Addition</u>
NaOH	47.49	72.80	20.08	140.37
K ₂ CO ₃	3.49	--	--	3.49
CaO	--	4.94	13.75	18.69
Na ₂ B ₄ O ₇	31.15	47.81	9.09	88.05
NaF	19.52	30.03	11.12	60.67
Totals	101.65	155.58	54.04	311.27

(311.27 = solids 278.56 + volatiles 32.71)

Desired slag composition (%)

	<u>Mixes 1 & 2</u>	<u>Mixes 3, 4 & 5</u>	<u>Mix 6</u>
SiO ₂	32.23	32.09	32.68
Al ₂ O ₃	17.37	17.29	17.61
B ₂ O ₃	9.86	9.83	5.12
Na ₂ O	28.11	27.99	21.92
K ₂ O	1.09	--	--
CaO	0.95	2.42	12.15
MgO	0.35	0.35	0.36
Fe ₂ O ₃	1.11	1.11	1.13
NaF	8.93	8.92	9.04

Smelting Results

<u>Heat</u>	<u>Charge</u>	<u>Total Pour</u>	<u>Ingot</u>	<u>Slag</u>
7	68.040	56.702	3.437	53.265
8	68.040	59.488	6.128	53.360
9	68.040	58.024	4.263	53.761
10	68.040	46.861	4.577	42.284
11	68.040	61.598	3.981	57.617
12	61.288	49.920	3.831	46.089
13	66.077	56.857	4.229	52.628
14	66.499	60.312	4.921	55.391
15	68.040	60.043	4.815	55.228
16	68.040	58.642	4.942	53.700

Table 6 (Continued)

Smelting Results

<u>Heat</u>	<u>Charge</u>	<u>Total Pour</u>	<u>Ingot</u>	<u>Slag</u>
17	65.945	55.279	4.581	50.698
18	72.000	62.354	5.029	57.325
19	<u>68.784</u>	<u>58.950</u>	<u>4.693</u>	<u>54.257</u>
	876.873	745.030	59.427	685.603
20	Clean-up heat ^a		<u>+0.992</u>	<u>-0.992</u>
Totals	876.873	745.030	60.419	684.611

Expected Materials Balance

$$\begin{aligned}\text{Stripped AgX } 567.84 &+ \text{flux } 311.27 = 879.11 \\ \text{Slag } 677.75 &+ \text{Ag } 55.65 + 145.71 \text{ volatiles} = 879.11\end{aligned}$$

a. Clean-up heat remelted silver-rich slag from Heats 12 through 19. Recovered silver was deducted from slag weight.

The materials balance resulting from smelting the stripped AgX did not match expectations as well as it did when smelting the AgX fines. The comparison is at the bottom of Table 6. Nearly 5 kg more of silver and 7 kg more of slag were recovered than the estimates indicated. These discrepancies are attributed to nonuniform stripping by ion exchange and variations in moisture content due to different drying times. It appears that the average moisture content of the 568 kg batch was 17.8% instead of 19.9%, and the silver was 10.6% instead of 9.8%. The errors are attributed to faulty sampling; however, no convenient means was available at the facility to obtain a more representative sample. Also, the AgX was not weighed originally, before ion exchange processing, so there was no firm basis for estimating total recovery efficiency from ion exchange and smelting processing.

Smelting of LOFT AgX

The LOFT facility had been storing about 700 lb (318 kg) of unserviceable AgX that had been used in chemical hood exhaust systems and was not radioactively contaminated. LOFT personnel offered this AgX for processing to

recover the silver when they learned of the success with recovering silver from the PBF AgX.

The LOFT AgX arrived in two drums. Samples of each drum were tested and found to have different water and silver contents. The drums were treated as distinct lots and designated as Barrel 1 and Barrel 2. Weighing the drum contents showed that 652 lb (296 kg) were received. The drying tests indicated water contents of 7.2 and 16.4%, while the smelting assays showed silver contents of 36.27 and 32.81%, respectively, on the as-received weight. Based on the smelting assay results, if 100% of the silver were recovered from the 296 kg, a total of 100.8 kg of silver would be reclaimed.

Ceramic grade CaF_2 was purchased to provide an opportunity to compare the relative effectiveness of CaF_2 and NaF as flux additions. A flux very similar to the mix given on page 22 was formulated and NaF and CaF_2 were substituted for each other on a weight-for-weight basis. The two lots were divided into three batches so that these fluorides could be compared separately as well as in combination.

Some refining of crude silver from the AgX fines and the stripped AgX had been done before the LOFT AgX arrived. This work disclosed that a 12-kg melt of silver filled a #8 crucible uncomfortably close to the top, so the charges of LOFT AgX were arranged to produce crude ingots weighing no more than 12.5 kg. Since both lots of LOFT AgX were richer in silver than the AgX melted previously, the maximum smelting crucible charge was restricted to between 51 and 55 kg so as not to produce ingots too large for a refining crucible. The combination of the smaller charge and the more effective flux reduced melting time considerably. The crucible used for melting Heats 11 through 20 was replaced to avoid introducing radioactivity into an otherwise clean slag, and because inspection indicated it was near the end of its useful life. The absence of radioactivity in the LOFT AgX eliminated the need for a HEPA filter, reducing expense while greatly improving the effectiveness of the exhaust hood.

Very little was changed in the charging and melting procedures developed during previous work, except that smelting proceeded so well with the smaller

charges and the improved flux that overtime was used so that the next day's heat could be entirely melted the night before and two pours could be made on the next day's shift instead of one. Heats 23 through 26 were made on a two-per-day basis. Some burner restraint was required after charging into a hot crucible, because even with the improved flux, rapid evolution of water vapor would produce enough foaming to threaten overflow. Also, it appeared that two pours per day may have rushed the process to the extent that the silver droplets did not have enough time to settle, for more silver shot was entrapped in the slag, particularly in the region just above the ingot.

Analyses of the slags are reported in Table 7, in parentheses, under slag composition. The nonradioactive slag provided opportunities for study heretofore unavailable. First, EDS chemical analyses could now be done inexpensively; second, the silver-rich slag was not accumulated for an additional melt to recover the silver. Instead, all of the slag from each heat was crushed and the shot was separated and weighed so that a more meaningful figure for process efficiency could be obtained.

A laboratory jaw crusher was used for comminution of the slag. The crusher was moved outdoors and operated when the wind was blowing. The crushed slag fell into a bucket while the wind blew the slag fines to the side. The crusher jaws were then adjusted to the minimum and the slag was cycled repeatedly through the crusher until one heat of slag was reduced to $\frac{3}{4}$ to $\frac{1}{2}$ bucket. This residue was treated in a gold pan until only silver shot remained. The shot was dried, weighed, and stored for the refining step.

Except for the quantity of slag, the predictions for the outcome of smelting the LOFT AgX were quite accurate. The weight of silver recovered from each heat is now "Ingot + Shot". The total silver reclaimed times the 99.1% figure for converting crude ingots into refined silver indicates 101.6 kg reclaimed, which is very close to the 100.8 kg predicted, based on the smelting assay. The quantity of shot extracted from the slag was 3.9% of the total, including an unusually large amount of shot recovered from Heat 26.

Table 7. Summary, smelting of LOFT AgX (all weights in kg)

LOFT AgX

	<u>Barrel #1</u>	<u>Barrel #2</u>	<u>Total</u>
Total AgX	142.184	149.637	291.821
Less 7.2%, 16.4% H ₂ O	-10.180	-24.546	-34.726
Less 36.27%, 32.81% Ag	-51.570	-49.246	-100.816
Refractory to be fluxed	80.434	75.845	156.279

<u>Flux</u>	<u>Mix 1</u>	<u>Mix 2</u>	<u>Mix 3</u>	<u>Total</u>
NaOH	23.84	23.66	17.51	65.01
CaO	10.43	10.34	7.69	28.46
Na ₂ B ₄ O ₇	7.58	7.53	5.57	20.68
CaF ₂	10.43	--	3.83	14.26
NaF	-----	10.34	3.83	14.17
Totals	52.28	51.87	38.43	142.58

(142.58 = Solids 127.94 + volatiles 14.64)

Desired (Obtained)^a Slag Composition (%)

	<u>Mix 1</u>		<u>Mix 2</u>		<u>Mix 3</u>	
SiO ₂	30.65	(35.49)	34.62	(36.21)	31.66	(35.96)
Al ₂ O ₃	17.41	(17.72)	17.11	(18.30)	16.96	(17.78)
B ₂ O ₃	5.25	(4.43)	5.07	(4.73)	5.00	(4.71)
Na ₂ O	20.81	(19.95)	20.08	(16.90)	20.01	(18.87)
CaO	10.43	(10.93)	10.06	(10.05)	10.05	(10.35)
MgO	2.09	(1.12)	1.13	(1.18)	1.61	(1.12)
Fe ₂ O ₃	2.49	(0.51)	1.80	(ND)	2.12	(ND)
CaF ₂	10.43	(9.03)	--	--	5.00	(5.14)
NaF	--	--	10.06	(11.70)	5.00	(5.26)

Smelting Results

<u>Heat</u>	<u>Charge</u>	<u>Total Pour</u>	<u>Ingot</u>	<u>Shot</u>	<u>Ingot + Shot</u>	<u>Slag</u>
21	51.198	45.675	12.374	0.126	12.500	33.175
22	51.198	46.055	12.394	0.132	12.526	33.529
23	51.198	45.898	12.298	0.103	12.401	33.497
24	54.627	45.911	12.064	0.512	12.576	33.335
25	54.627	46.785	11.935	0.362	12.297	34.488
26	54.627	46.481	10.956	1.446	12.402	34.079
27	52.765	46.670	12.101	0.519	12.620	34.050
28	52.765	46.556	12.231	0.689	12.920	33.636
29	10.920	9.633	2.203	0.088	2.291	7.342
Totals	433.925	379.664	98.556	3.977	102.533	277.131

Expected Materials Balance

LOFT AgX 291.82 + flux 142.58 = 434.40
 Slag 284.21 + Ag 100.82 + volatiles 49.37 = 434.40

a. Numbers in parentheses are slag analysis results.
 ND = not detected.

Refining of Crude Silver

The furnace and accessories used to convert the crude silver ingots from the smelting process into marketable refined ingots are shown in Figure 5 and a general description of the equipment and the refining procedure is given on pages 27 to 32.

The normal working capacity of the #8 crucibles was about 11 kg of silver, but 12.44 kg is required to produce four bars of 100 troy ounces each. This much silver filled the crucible to within $\frac{1}{4}$ in. (2 cm) of the top. The crucibles were quite heavy and pouring would begin after only a small amount of tilting, so some care was necessary when pouring the first ingot to avoid spillage.

An oxygen lance was constructed by modifying a standard acetylene torch tip to accept a section of stainless steel tubing with a fitting to hold a 6 in. (15 cm) piece of 2-hole alumina thermocouple tubing. The alumina tubing was to be inserted into the melt, but the melt surface was so near the top of the crucible that the emerging bubbles would spatter silver droplets into the furnace. So the oxygen lance was positioned just above the melt, and the oxygen pressure was regulated to provide a jet that pressed a large dimple into the melt surface. This was effective. To deoxidize the silver, a carbon rod was weighted on the upper end so that it would not float and inserted into the melt to react with the oxygen. Also, the fuel/air ratio for the burner was adjusted to "rich" to provide a reducing atmosphere. When evolution of small CO_2 bubbles ceased, the silver was deoxidized.

A mix of $\frac{1}{2}$ silica and $\frac{1}{2}$ anhydrous borax was used as a refining flux. This mix was quite viscous at the refining temperature and would adhere readily to a cool steel rod contacting it. A steel disc was welded to the slag-dipping rods to pick up more slag and hasten the removal process. Five such rods were made. The dipping rods with slag attached were dropped in a steel container to cool, and a fresh dipper would be used. When the dippers cooled, the adhering slag could be broken away easily by tapping the disc against the side of the container. If the dippers were used with care so that they touched the

slag surface only and were not submerged in the metal, the slag could be removed completely from the melt surface without carrying away silver.

If the crude ingot contained a large amount of entrained smelting slag, a charge of refining flux would be added to remove this material before refining began. The smelting slag was too fluid to be removed easily by the dippers if not diluted by the high-silica refining flux. When refining with oxygen, the oxidized impurities would float to the surface and form a thin film. Enough refining flux was added to cover the melt surface and it remained there until it fused. The metal oxides reacted with the flux and formed metal silicates, which were soluble in the slag but not in the molten silver. Lancing and fluxing was continued until the film would not form on the melt. Two cycles were usually sufficient.

The iron impurity in the AgX was a problem. This metal would be reduced by the crucible carbon and eventually form Fe_3C . The Fe_3C would follow the silver into the ingot pocket and float on the ingot surface. The Fe_3C buttons were difficult to oxidize during refining and required a substantial amount of oxygen and refining flux. The best approach found was to remove the largest buttons mechanically from the ingots by driving a punch at an angle into the ingot surface just beneath the buttons and popping them out, or by plucking them from the melt surface with tongs.

When the silver was judged to be refined and deoxidized, the burner was shut off and the door opened. The crucible was then removed manually with the tongs and the silver poured into four molds. This operation is shown in Figure 8; several crude ingots are located at the lower right of the photo, a crude ingot is in a crucible in front of the operator, and the refined ingots are stacked at the lower left edge of the photo. The operator is pouring an assay pin before filling the fourth ingot mold. The torch lying across the crude ingots in Figure 8 was used to "melt-in" the surfaces of the solidifying ingots to avoid development of surface "sinks" and shrinkage cavities.

Mold Cote™, the same release agent used in the pouring receptacle, was applied to the 100-oz ingot molds so that the ingots could be shaken out. Dipping warm molds into the release agent and hanging them up to dry gave a

Figure 8. Pouring 100-tr oz ingots of refined silver.

through the tub. Identity numbers were stamped on the ingots as soon as they were retrieved from the acid. The assay sample was identified, placed in a small bottle, and stored with the ingots in the vault. Later, the ingots were weighed, and their weight, in grams and troy ounces, and their source were stamped into the surface. The heat identification and the corresponding weights are given in Table 8.

Refined Silver Chemistry

The early assay samples were obtained by pouring the last of the crucible contents into a pail of water, producing shot. This practice was not wholly satisfactory. The operator could not see how much silver remained in the crucible after pouring the last ingot. Too large a sample would boil the water, while at the other extreme, some samples were barely enough for assay. The assay pin mold in the modified tongs was devised to solve this problem, and is shown being filled in Figure 8 prior to pouring the last ingot. Wire cutters could snip a suitable sample from the assay pin, and the balance of the pin was saved in case a recheck was necessary.

Some samples among the first set of assays puzzled the assayer, as they showed a higher purity than his standard. Rechecking verified this result. Subsequent samples of refined silver were submitted to the assayer as well as to a laboratory with atomic absorption (AA) equipment. This time the assayer reported his results to three figures only. These data and the AA results are given in Table 9. The impurities detected were totalled and subtracted from 100% to produce the result in the last column. Other impurities, if present, were below the AA detection limit. When refining was completed, the ingots were stacked and photographed. They are shown in Figure 9.

Table 8. Refined silver production

Heat & Ingot	Ingot		Heat & Ingot	Ingot		Heat & Ingot	Ingot	
	Grams	Troy Oz		Grams	Troy Oz		Grams	Troy Oz
1 - 1	3061.6	98.4	7 - 1	3255.6	104.7	13 - 1	3171.3	102.0
- 2	3030.4	97.4	- 2	3196.1	102.8	- 2	3015.5	97.0
- 3	3129.4	100.6	- 3	3269.2	105.1	- 3	3198.4	102.8
- 4	3141.7	101.0	- 4	2729.0	87.7	- 4	3038.9	97.7
	<u>12363.1</u>	<u>397.4</u>		<u>12449.9</u>	<u>400.3</u>		<u>12424.1</u>	<u>399.5</u>
2 - 1	3036.1	97.6	8 - 1	3091.6	99.4	14 - 1	3093.0	99.4
- 2	3202.2	103.0	- 2	2973.5	95.6	- 2	3283.1	105.6
- 3	3183.6	102.3	- 3	3188.5	102.5	- 3	2965.7	95.3
- 4	3147.6	101.2	- 4	2954.2	95.0	- 4	2949.3	94.8
	<u>12569.5</u>	<u>404.1</u>		<u>12207.8</u>	<u>392.5</u>		<u>12291.1</u>	<u>395.1</u>
3 - 1	3090.5	99.4	9 - 1	3136.9	100.9	15 - 1	2952.1	94.9
- 2	3244.4	104.3	- 2	3301.8	106.2	- 2	3016.6	97.0
- 3	3131.9	100.7	- 3	3138.7	100.9	- 3	3239.5	104.2
- 4	3007.8	96.7	- 4	2877.4	92.5	- 4	3151.5	101.3
	<u>12474.6</u>	<u>401.1</u>		<u>12454.8</u>	<u>400.5</u>		<u>12359.7</u>	<u>397.4</u>
4 - 1	2946.0	94.7	10 - 1	2896.1	93.1	16 - 1	3108.0	99.9
- 2	3150.0	101.3	- 2	3258.3	104.8	- 2	3187.8	102.5
- 3	3136.1	100.8	- 3	2875.4	92.4	- 3	3283.9	105.6
- 4	3151.8	101.3	- 4	3173.7	102.0	- 4	2757.7	88.7
	<u>12389.9</u>	<u>398.1</u>		<u>12203.5</u>	<u>392.3</u>		<u>12337.4</u>	<u>396.7</u>
5 - 1	3284.7	105.6	11 - 1	3175.0	102.1	17 - 1	3033.0	97.5
- 2	3241.7	104.2	- 2	3169.2	101.7	- 2	3158.7	101.6
- 3	3364.3	108.2	- 3	3252.2	104.6	- 3	3142.8	101.0
- 4	2611.1	83.9	- 4	2830.7	91.0	- 4	3078.0	99.0
	<u>12501.2</u>	<u>401.9</u>		<u>12420.8</u>	<u>399.4</u>		<u>12412.5</u>	<u>399.1</u>
6 - 1	3110.9	100.0	12 - 1	3012.4	96.9	18 - 1	3017.8	97.0
- 2	3166.8	101.8	- 2	3208.9	103.2	- 2	3018.7	97.1
- 3	3236.2	104.0	- 3	3222.1	103.6	- 3	1046.2	33.6
- 4	2941.6	94.6	- 4	2888.9	92.9	---	-----	-----
	<u>12455.5</u>	<u>400.4</u>		<u>12332.3</u>	<u>396.6</u>		<u>7082.6</u>	<u>277.7</u>

Table 9. Refined silver assay and analytical data

Refining Heat Number	Fire Assay (%Ag) ^a	Atomic Absorption Analysis (ppm)					% Ag (by diff.)
		Cu	Fe	Pb	Ni	Zn	
1	99.91						
2	99.90						
3	99.99						
4	99.89						
5	99.90			No Samples Submitted			
6	99.91						
7	99.98						
8	99.58						
9	99.99						
10	99.9	22.0	6.2	24.0	6.7	5.7	99.994
11	99.9	11.0	46.2	21.0	16.0	4.3	99.990
12	99.9	10.0	9.5	20.0	7.5	17.0	99.994
13	99.9	15.0	30.0	14.0	49.9	25.0	99.987
14	99.9	17.0	4.0	23.0	19.0	14.0	99.992
15	99.9	60.1	20.0	99.7	33.0	9.6	99.978
16	99.9	17.0	8.6	9.6	7.6	5.7	99.995
17	99.9	15.0	28.0	4.8	11.0	9.6	99.993
18	99.9	87.2	74.4	61.7	69.1	20.0	99.969
Smelting Heat							
Number							
22	----	11.0	848.	7.9	13.0	33.0	99.909
25	----	16.0	677.	33.0	14.0	55.9	99.920
27	----	11.0	682.	19.0	18.0	45.0	99.923

a. Assays by Specomp Services - Boise Lab, Boise, Idaho.

Figure 9. Assembled refined silver ingots.

DISCUSSION

The preceding sections each contain a discussion of experiments and experiences that led to a result, and that information need not be reviewed in detail here. The project was product-oriented, and time and funding were limited. The end result was satisfactory, but not necessarily optimum. The project was very successful in terms of the primary objective: to develop a process that recovered as much silver as possible from unserviceable and radioactively-contaminated silver zeolite. A number of questions arose during the course of the work for which no answers were apparent, for which there were no resources for study when these uncertainties were not critical-path problems, and which could have created distractions with regard to keeping the primary objective in view. The answers to some questions became evident during the review of the data and the excogitation that eventually led to this report. Some answers may be confirmed when more AgX becomes available for processing. Resolution of other questions must wait for another day.

Equipment, General

The equipment used for this project has been excessed. Presently, the total INEL inventory lists 4674 kg (10,304 lb) of AgX¹⁷ containing an estimated 1640 kg (3600 lb or 52,700 tr oz) of reclaimable silver. This process should recover at least 97% of this amount. While it is unlikely that the total inventory will be released in one batch for processing, collections of excess AgX will likely be substantial and would warrant purchase of larger and more efficient equipment that should be installed in a facility specifically designed for this work. The recommendations that follow are the product of accumulated hindsight.

Induction melting is more energy efficient than propane and does not produce the large volume of combustion-product gas. An induction unit capable of delivering between 30 and 50 kW would be suitable for duplicating the capacity of the propane-fired furnace. If a larger induction unit is to be considered, it should be sized to handle a 150 kg (330 lb) charge and produce a 32 kg crude silver ingot to increase the refining heat size to 1000 tr oz.

Such a unit would require a 100 kW power supply^a which could bring the charge to pouring temperature in less than 3 h if outgassing would permit heating at such a rate. The increased equipment cost would be easily offset by savings in labor charges, as the total inventory could be processed in 52 rather than 135 heats. Used motor-generator units are relatively inexpensive in view of the trend toward the quiet solid-state power supplies; however, the solid state power supplies are compact, versatile, and much more energy efficient. The refining furnace would be coupled to the same power supply used by the smelting furnace.

The pyramidal ingot-slag mold used for this project should be replaced with a conical slag mold that produces a cylindrical ingot of crude silver. The pyramidal shape did not handle the stresses resulting from a pour of 1200°C slag and silver well, and distorted after a number of pours -- the mold legs would then bind on the locating pins, and the container had to be pounded back into shape. The conical slag-containing portion of the new design could nest into a conforming conical ring that would be attached to the connecting link to the furnace body. The ingot pocket would be cylindrical and sized to produce an ingot that conformed well to the refining crucible. The round ingot top would provide a smaller area from which to remove large buttons of iron carbide.

A HEPA-filtered exhaust system would have drops to each furnace and be connected to the dust hood used for handling charges. A wet scrubber ahead of the HEPA filter would greatly prolong filter life; the scrubber cost could be recovered by not having to replace 6 or 7 filters. The captured particulates, which contain some silver, would be recovered as a sludge, dried, and charged back into the smelting furnace.

Smelting Crucibles

The attributes of the carbon-bonded, silicon carbide crucibles enabled this project to succeed with the aggressive flux compositions needed to render

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a. C. R. Eckert, private communication, Inductotherm Corporation, Rancocas, NJ, July 15, 1988.

zeolites tractable. Fireclay crucibles, with a composition similar to zeolite, would have been rendered similarly tractable, and other ceramic compositions would not have fared much better. A silicon carbide crucible lasted about 10 smelting heats with the practice described before the walls became so thin that further use would risk sidewall penetration by the slag and require reconstruction of the crucible cavity.

Two modifications to the procedure may contribute significantly to longer crucible life, blending carbon into the flux mix and drying all of the AgX at 600 to 700°C. Oxygen is evolved during the destruction of the AlO_4 tetrahedra. The iron impurity in the zeolite becomes iron carbide. Both reactions occur at the expense of the carbon bond of the crucible. Since the quantities of these components are known from the chemical analysis of the AgX, enough carbon should be added to the flux to react with the oxygen as well as to form iron carbide from the oxide, thereby relieving the crucible of the burden of supplying this carbon. Use 75 g carbon black for each kg of Al_2O_3 in the charge and 180 g for each kg of Fe_2O_3 .

Evolution of water vapor causes foaming during melting, and although little chemical reaction occurs, mechanical damage results from bubble action, particularly at the slag-air interface. Loss of agitation within the slag may reduce the tendency of silver to form droplets large enough to settle quickly, but stirring of the melt by induction currents, plus reaching 1300°C more quickly and maintaining the melt longer at the temperature where the slag is more fluid should more than compensate for the loss of gas agitation. Fully dried AgX may be easier to handle during weighing and blending.

The crucibles for induction melting will require external refractory support, a restriction that applies to both smelting and refining crucibles and which would make the crucibles much more difficult to replace. Instead of simply lifting out an expended crucible and lowering a new one into its place, as was done with the propane-fired furnace, the induction unit would require breaking out the old crucible with a hammer and removing all the backup material. After inspecting the cement supporting the induction coil and patching, if necessary, the new crucible would be installed and the supporting refractory rammed into place. If production requirements cannot tolerate such

delays, an additional furnace body should be purchased so that the new crucible may be installed, baked out, and standing by, ready for production.

Refining Crucibles and Refining Processes

The refining crucible is used primarily to contain the silver while the impurities are oxidized, and little protection is required from the aggressive slag. The silicon carbide vessel could be lined with a durable ceramic to assure that the refining environment was more oxidizing. The purity of the refined silver might be even better if the injected oxygen was not required to compete with the crucible carbon when attempting to remove difficult-to-oxidize impurities, such as copper.

The purity of the crude silver ingots, as shown at the bottom of Table 9, is equivalent to "bullion" or "commercial bar"¹⁸. Simply remelting these ingots to remove traces of radioactive slag and the floating buttons of iron carbide, and then casting them directly into 100-oz bars might be adequate. The impurities present may have been carried into the AgX by the silver nitrate during the ion-exchange conversion of AgX, as the specification for this reagent allows impurity levels in the range encountered in the crude ingots. At these low impurity levels, the oxygen refining step would not be necessary. In the event that unserviceable AgX is contaminated by tramp metal, the impurity level would be higher than permitted by the cited ASTM specification. If the oxygen-refining step had not been routinely employed, the ingots would require remelting and refining after the assay report was received. In Table 9, smelting Heats 22, 25, and 27 became refining Heats 11, 14, and 16, respectively. The most significant purity improvement resulted from the removal of Fe, Zn, and Pb, while Ni and Cu were reduced only slightly, if at all. The possibility exists that the Ni and Cu impurities were oxidized and then reduced again by the crucible before they could be removed in the slag. For this reason, and also to reduce crucible attrition from the oxygen jet, a suitable oxide liner for the refining crucible should be sought.

Slags

Questions regarding the suitability of the slag compositions selected for this work are numerous and answers are elusive. The U.S. Bureau of Mines (USBM) has studied a variety of slag compositions including some containing fluorides.^{15,19-23} The USBM efforts focused on ferrous smelting and a higher temperature regime than was used in this project. Nonetheless, these works are useful as a foundation to underlie needed future studies. Recent emphasis on secondary slag treatment to recover lost metal values, and the need to reduce energy requirements of pyrometallurgical processes are but two of the areas needing study.

The slag compositions used for this work were effective in that 97% of the silver could be recovered from the AgX. Two to three percent of the silver was entrained in the slag as shot. Considering the 1200 to 1300°C temperatures used for this work, slag fluidity was adequate. The early studies of composition vs. fluidity were somewhat primitive, but they enabled the objective to be attained with limited resources.

A better Na₂O/CaO ratio for aluminosilicate slags should be sought. It is likely that the quantity of CaO could be increased beyond 12% and permit a reduction of Na₂O, resulting in less water evolving from decomposing NaOH. In this regard, small quantities (<5 wt%) of other inexpensive oxides that will not be reduced by crucible carbon at process temperatures deserve consideration also. More precise slag formulation may have permitted reducing the process temperature.

A rationale for studying composition vs. fluidity is contained in an INEL study unrelated to this project.²⁴ This work established a data base to model a number of slag compositions in order to predict viscosity. Unfortunately, fluorides were not included in the data base. Continuation of this effort and expanding the data base to include fluorides would reduce the cost of an empirical study. The potential for energy and resource conservation for the domestic nonferrous metals industry may be significant.

Economics

Gathering data to permit an economic evaluation of the project was a lower-priority item, certainly secondary to assimilation of technical data. Some data were gathered during the recovery of silver from the LOFT AgX, but these should be considered preliminary in nature as they were obtained to facilitate providing an estimate for the next batch of AgX to be treated and assumed that the same process would be used in the same equipment by the same personnel.

The project cost from start to finish was \$97,440, covering the experimental development of the process, the design and construction of the equipment, and the production effort that recovered the 7000 tr oz of silver shown in Figure 9. This cost did not include nonchargeable overtime, the items scavenged from the scrap yard, nor the equipment that was already in place that was used or modified for use for this project. When the price of silver was \$13.92/tr oz, the project broke even.

Based on the limited data obtained, and operating under the conditions given above, it would cost \$15,049 to recover 4700 tr oz of silver from a 1000-lb batch of unserviceable, radioactively-contaminated AgX, or about \$3.20/tr oz. Labor hours (258 h @ \$52/h) constitute 89% of this cost. Perhaps a more meaningful way to express the cost would be: Cost per tr oz = \$0.35 for materials and maintenance + 0.055 man-hr. Obviously, once the operating parameters of the process are firmly established, the opportunities for operating economies become numerous. The alternative costs for disposal, regeneration, or replacement of unserviceable AgX were not considered.

SUMMARY

This project uncovered little that was new about the metallurgy of silver, which was not unexpected as silver has been an object of study for four millennia. Several traditional techniques were approached in a new way, but usually as a matter of convenience and not in the spirit of innovation. Several aspects of this project were innovative, however. The availability of carbon-bonded silicon carbide crucibles enabled the use of the very aggressive flux required to convert the aluminosilicate zeolite structure into a fluid slag at temperatures below 1200°C. Also, the use of sodium hydroxide flakes as a source of Na₂O in preference to soda ash in order to reduce foaming was innovative. Of course, this substitution was permitted by the silicon carbide crucibles, yet the NaOH worked so well and its applicability seemed so obvious that the writer was surprised that no reference could be found regarding the use of NaOH in this manner. This application of NaOH is one of the claims in Patent 4,564,391, "Method for the Recovery of Silver from Silver Zeolite".

Once the initial barriers were overcome, the recovery of silver from AgX became a routine smelting operation, and the experimental phase was transformed into a production-oriented pilot plant operation. While data acquisition concentrated on routine record keeping for materials balance purposes, experimentation continued through the pilot plant phase, including the last smelting and refining heats. In all, 29 smelting heats and 18 refining heats were used to recover the silver from three batches of AgX totalling 1048 kg. Table 10 is a summary of the materials balances of the project, and includes data extracted from Tables 5, 6, and 7.

The most suitable flux produced a slag of the following composition:

<u>Component</u>	<u>wt%</u>	<u>Component</u>	<u>wt%</u>
SiO ₂	32	CaO	12
Al ₂ O ₃	17	MgO	2
B ₂ O ₃	5	Fe ₂ O ₃	2
Na ₂ O	20	CaF ₂	10

Table 10. Production summary (all weights in kg)^a

<u>AgX</u>				
	<u>Total</u>	=	<u>H₂O</u>	+ <u>Ag</u> + <u>Refractory</u>
Fines	182.8		28.9	54.9 99.1
Stripped	567.8		113.0	55.7 399.2
LOFT	<u>291.8</u>		<u>34.7</u>	<u>100.8</u> <u>156.3</u>
Totals	1042.4 ^b		176.6	211.4 654.6
<u>Flux</u>				
	<u>Total</u>	=	<u>Solids</u>	+ <u>Volatiles</u>
Fines	83.3		75.6	7.7
Stripped	311.3		278.6	32.7
LOFT	<u>142.6</u>		<u>127.9</u>	<u>14.6</u>
Totals	537.2		482.1	55.0
<u>Smelting Results</u>				
	<u>Charge</u>	<u>Total Pour</u>	<u>Ingot</u>	<u>Slag</u>
Fines	265.8	225.9	56.2	170.2
Stripped	876.9	745.0	60.4	684.6
LOFT	<u>433.9</u>	<u>379.7</u>	<u>102.5</u>	<u>277.1</u>
Totals	1576.6	1350.6	219.1	1131.9
Total Refined Silver = 217.7 kg, ratio, refined:crude = 0.994				
<u>Materials Balance</u>				
	<u>AgX + Flux</u>	=	<u>Slag</u>	+ <u>Ag</u> + <u>Volatiles</u>
Predicted	1579.6		1136.7	211.4 231.6
Obtained	1576.6		1131.9	217.7 227.0

a. Some column totals may not agree due to rounding.

b. Total AgX less smelting samples.

CaF₂ was preferred to NaF, or a combination of the two, because more iron remained in the slag when CaF₂ alone was used. A need for a more quantitative study of slags was noted earlier.

Numerous areas for additional study were uncovered during the course of this work and resolution of some of these questions may have impact far beyond the limited scope of this study. One area concerns the potential use of AgX beds to replace the charcoal units presently in service in commercial power reactors. The efficiency and the economies of the AgX units have been demonstrated at the INEL, although two sources of reluctance are apparent here: (1) The tie-up of capital in value of the silver, and (2) the inability of AgX to capture the radioactive noble gases. Availability of the subject process should assure that the silver tied up in the AgX beds is, in effect, in storage rather than lost, and other varieties of zeolite are known to have an affinity for noble gases.

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