

LA-10681

UC-10

Issued: July 1986

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LA--10681

DE86 014881

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THE PREPARATION OF FUSED CHLORIDE SALTS FOR USE IN PYROCHEMICAL PLUTONIUM RECOVERY OPERATIONS AT LOS ALAMOS

by

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ABSTRACT

The Plutonium Metal Technology Group at Los Alamos routinely uses pyrochemical processes to produce and purify plutonium from impure sources. The basic processes (metal production, metal purification, and residue treatment) involve controlling oxidation and reduction reactions between plutonium and its compounds in molten salts. Current production methods are described, as well as traditional approaches and recent developments in the preparation of solvent salts for electrorefining, molten salt extraction, lean metal (pyroredox) purification, and direct oxide reduction.

I. PLUTONIUM PYROCHEMISTRY AT LOS ALAMOS

The Plutonium Metal Technology Group (MST-13) routinely recovers pure plutonium metal from impure scrap sources using chemical or electrochemical oxidation and reduction reactions in molten chloride solvent salts.

Each of these batch pyrochemical operations requires a unique salt matrix that can act as reaction media, a reactant, or a solvent for impurities. The volume of salt for each of the batch operations is large, relative to the amount of plutonium in the process, and the quality of the feed salts is extremely important. Measures of quality include moisture content, oxygen content, and the concentration of elemental impurities. Low-quality salts result in low process yields, low product quality, and increased operational costs.

This report summarizes the preparation requirements for reagent- and food-grade salts used in plutonium metal production at Los Alamos. We first discuss the major metal production steps and the role of each salt in those steps. We then describe salt preparation; and finally, we discuss our development efforts for improved salt preparation.

II. PLUTONIUM METAL PRODUCTION, PURIFICATION, AND RESIDUE TREATMENT

The pyrochemical operations at Los Alamos can be broken down into three basic categories—metal production, metal purification, and residue treatment. Figure 1 is a flow diagram of the various process steps. The following paragraphs discuss these steps and the roles of salt reagents.

A. Metal Production

Two major metal production operations are used to convert PuO_2 to plutonium metal—the classical bomb reduction, or PuF_4 reduction step,¹⁻⁵ and the direct reduction of PuO_2 to metal.^{1,2,5} Both processes consist of chemically reducing plutonium compounds to plutonium metal with no purification of the metal occurring.

In PuF_4 reduction, PuO_2 is first fluorinated with HF to PuF_4 . This compound is mixed with iodine and calcium metal, then heated in an induction furnace to initiate the reactions. Both the iodine and PuF_4 reactions with calcium are very exothermic; the waste slag (CaI_2 and CaF_2) melts, allowing the plutonium metal to

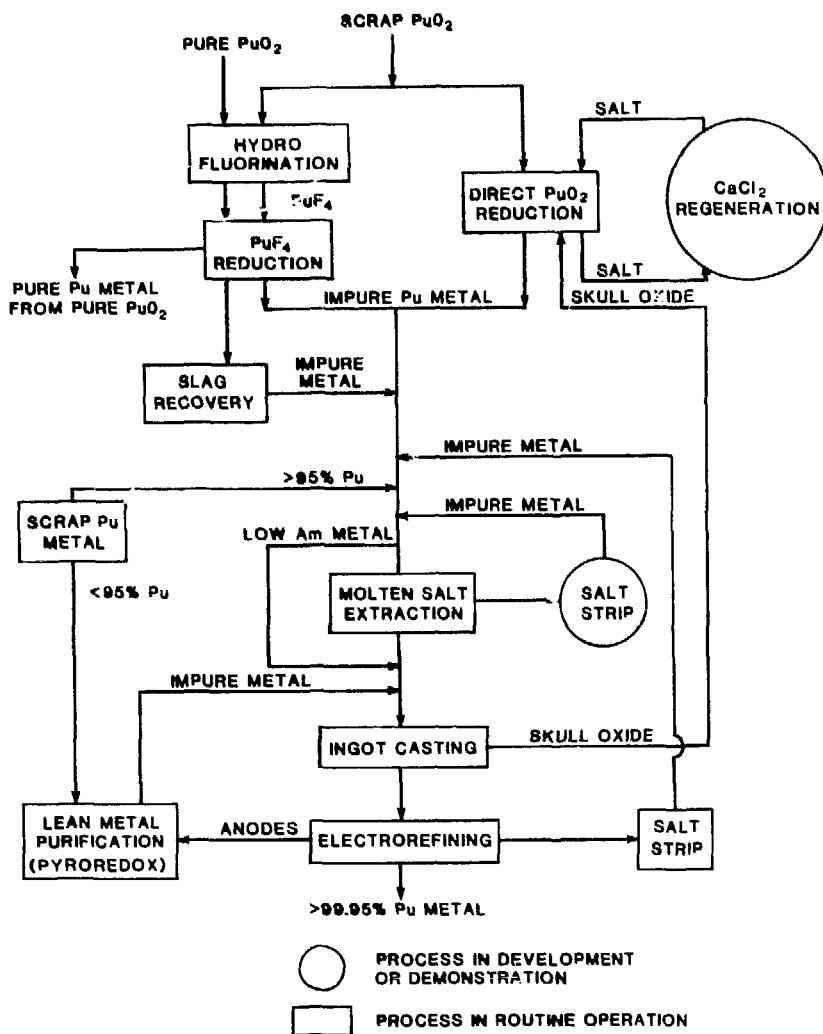


Fig. 1. Plutonium pyrochemical operations at Los Alamos.

coalesce in the bottom of the ceramic reaction vessel. Metal yields from this process normally exceed 98%.

Direct oxide reduction (DOR) converts PuO_2 to metal by reduction with calcium metal in a CaCl_2 solvent salt. The molten CaCl_2 not only acts as a heat sink during the exothermic reduction reaction and provides a medium in which to mix the reactants, it also dissolves the CaO by-product to 18 mol% (10 wt%), which aids in product metal coalescence. Metal yields from this process normally exceed 95%.

B. Metal Purification

Our purification process has two principal steps—molten salt extraction (MSE)^{1,6} and electrorefining (ER).^{1,7-9} In the MSE step americium is removed by

contacting molten plutonium metal with a molten oxidizing salt ($\text{MgCl}_2 \cdot \text{KCl} \cdot \text{NaCl}$)*. The MgCl_2 oxidizes americium and some plutonium into the salt phase, purifying the plutonium but with some loss. If the impure metal produced in either DOR or PuF_4 reduction contains >1000 ppm Am, the metal is sent through MSE. If the metal contains <1000 ppm americium, it bypasses MSE and proceeds to ingot casting.

Ingot casting is essentially a sizing operation to produce metal ingots for feed into electrorefining. Although the casting operation is performed under vacuum and some volatiles (Ca° , Mg°) are removed, it is not a true purification step.

Electrorefining is the main purification process performed at Los Alamos. It can produce kilogram

* ^{241}Pu decays to ^{241}Am at the rate of approximately 41 ppm/month/at. % ^{241}Pu .

quantities of plutonium metal with purity regularly exceeding 99.95%. The impure plutonium feed is slightly oxidized in an $MgCl_2 \cdot NaCl \cdot KCl$ electrolyte to charge the solvent with Pu^{3+} . During electrorefining plutonium is preferentially oxidized at an impure anode surface. From the anode, plutonium migrates through the solvent salt and is reduced at a separate cathode surface. As plutonium is depleted from the anode, impurities more electropositive than plutonium concentrate and eventually form solid plutonium alloys, inhibiting further oxidation of the plutonium. If not controlled, these impure alloys begin to oxidize instead of plutonium. We control the unwanted oxidation of impurities by periodically monitoring the open circuit potential or back-emf of the cell during the process. The process terminates when this potential increases to a predetermined value. Metal yields from electrorefining are normally 70-85% with 10-15% of the feed plutonium remaining in the anode. The remainder of the plutonium is unreduced $PuCl_3$ or uncoalesced metal shot in the salt phase.

C. Residue Treatment

Residues from DOR and PuF_4 reduction are mainly salts ($CaCl_2 \cdot CaO$ or $CaF_2 \cdot CaCl_2$) that occasionally contain enough uncoalesced or unreduced plutonium to justify pyrochemical reprocessing. The DOR salts may be reprocessed by adding $CaCl_2$ to dilute the CaO , and calcium metal to provide a reducing environment. We are currently demonstrating a regeneration technique for spent DOR salts that rechlorinates the CaO by-product and produces a $CaCl_2$ salt suitable for recycle to DOR.¹⁰

Plutonium may be effectively recovered from PuF_4 reduction slag by similar reprocessing¹¹ in which $CaCl_2$ is added to the crushed $CaF_2 \cdot CaCl_2$ slag to lower its melting point from 1320°C to 800°C. As with the DOR

salts, calcium metal is added to provide a reducing environment.

Residues from MSE contain significant quantities of plutonium (100-200 g) that are co-oxidized with americium. We can recover the oxidized plutonium and americium by reduction with calcium metal, but have yet to develop a suitable pyrochemical technique for separating the two metals. Current research is focusing on both chemical¹² and electrochemical¹³ separation techniques.

The electrorefining operation produces more residue than any other aspect of plutonium pyrochemistry. In addition to producing pure plutonium, electrorefining also generates rich waste salts and spent anodes. These salts are currently treated similarly to spent MSE salts¹⁴ by reduction with calcium metal. The spent anodes, however, require a more complex pyroredox process¹⁵ to separate the plutonium from the concentrated impurities. This process consists of selectively oxidizing plutonium with $ZnCl_2$ in a KCl diluent. The zinc and impurities more electropositive than zinc collect during plutonium oxidation. The K_3PuCl_6 salt phase is then mechanically separated from the zinc metal residue and reduced with calcium metal in a DOR-like step. The metal from this step contains a mixture of plutonium, calcium, and zinc from which the plutonium is separated by gravity. This plutonium concentrate is then suitable for electrorefining.

From this cursory overview of our pyrochemical operations, we see that large volumes and varieties of high-quality chloride-based solvent salts are required for plutonium metal production. Table I summarizes the salt requirements for the various pyrochemical processes.

Moist salts are detrimental because oxide formation adversely affects metal coalescence and recovery. Gross element impurities in the salts are detrimental because molten plutonium metal very effectively scavenges them, ultimately reducing electrorefining yields. Therefore, the reagent- or food-grade salts used in our

TABLE I. Salts Used in Plutonium Pyrochemistry at Los Alamos

| Process | Required Salt |
|---|--|
| PuF_4 reduction | - No added salt; it is generated in situ |
| DOR | - $CaCl_2$ |
| MSE | - $KCl \cdot NaCl \cdot MgCl_2$ or - $CaCl_2 \cdot NaCl \cdot MgCl_2$ |
| Ingot casting | - no added salt |
| Electrorefining | - $KCl \cdot NaCl \cdot MgCl_2$ |
| PuF_4 slag recovery | - $CaCl_2$ |
| MSE salt strip | - Possibly $CaCl_2$ |
| Electrorefining salt strip | - Possibly $CaCl_2$ |
| Pyroredox | - $CaCl_2$ and $ZnCl_2 \cdot KCl$ |

pyrochemical operations must be treated before use. Section III describes the treatment processes.

III. SALT PREPARATION

The goal of our pyrochemical operations is to recover and purify plutonium metal from impure feed streams. These operations require such large volumes of feed salts that we cannot justify the time or effort necessary to produce polarographic-grade salts (no water, water by-products, or metallic impurities). Although time-consuming and complex, there are established physical, chemical, and electrochemical techniques to produce polarographic salts suitable for electrochemical research.¹⁶⁻²⁰

Before 1983, plutonium feed streams at Los Alamos were well characterized and high quality. We enjoyed good process yields with minimal residue generation. Food-grade or reagent-grade salt preparation consisted of drying in vacuum ovens to dehydrate bulk hygroscopic salts (CaCl_2) and/or storing the salts under argon until used (KCl , NaCl , MgCl_2). CaCl_2 , used in DOR and salt stripping operations, was pressed into cylinders after drying to minimize the surface area-to-volume ratio for moisture absorption and also to increase its density, which simplified loading the salt into the processes.

Since 1983, however, pyroredox processing, which requires special preparation of the binary salt $\text{ZnCl}_2 \cdot \text{KCl}$, has been integrated into the recovery scheme. Also, feed PuO_2 for the DOR process has become more variable, is generally not well characterized, and is of lower quality. As a result, more care is required in preparing the CaCl_2 ; impurities (water or water by-products) affect the reduction reaction, the subsequent product metal coalescence, and ultimately, the process yield. The following sections describe the available salt preparation techniques and their effects on plutonium metal processing.

A. Electrorefining Salts

This process uses an equimolar mixture of NaCl and KCl as the solvent salt. Both of these salts are purchased as reagent-grade materials from a variety of chemical supply houses. They are not appreciably hygroscopic and are fused before use in electrorefining. Before fusing, the undried, as-received salts are mixed and placed in a quartz or platinum crucible. The salts and crucible are then placed in a stainless steel furnace tube, backfilled with purified argon, and resistance-heated to 750-800°C. After fusing, the mixture is cooled, removed from the crucible, and stored in a vacuum oven at 200°C until needed. This simple procedure allows production

of these salts on a demand basis. These salts provide trouble-free performance in the electrorefining operation. As the salts are loaded into an electrorefining run, 75 to 100 g of MgCl_2 are added as loose salt to oxidize plutonium and charge the electrolyte with Pu^{+3} .

B. Molten Salt Extraction (MSE) Salts

MSE uses fused equimolar $\text{NaCl} \cdot \text{KCl}$ (from ER salt production) with the addition of 300 to 500 g of loose MgCl_2 . The MgCl_2 is purchased from the Titanium Corporation of America and although the salt is hygroscopic, the only treatment is storage in glass containers to keep out excess moisture. No problems with metal recoveries or oxidation yields in MSE have been observed as a result of this minimal procedure.

To simplify and optimize MSE, the established feed salt ($\text{NaCl} \cdot \text{KCl} \cdot \text{MgCl}_2$) and an alternate salt mixture ($\text{CaCl}_2 \cdot \text{KCl} \cdot \text{MgCl}_2$) were separately fused in a process similar to that used for ER salts. The salts performed well, but because we do not routinely perform MSE, production of ternary salts was not adopted for the process.

The procedure for preparing the salt mixture entailed blending the three salts in an inert box and transferring them to a platinum or quartz crucible for fusing. The mixture was melted, sparged with argon to mix the components, vacuum-transferred,* and cast into a quartz mold where it cooled under argon. The quality of these two ternary fused salt mixtures are described in Table II.

C. Lean Metal Purification or Pyroredox Salts

Until the development of pyroredox (lean metal) purification, salt preparation for all pyrochemical processes was relatively simple. However, the ZnCl_2 used for upgrading lean metal residues is hygroscopic to the point of being deliquescent, and special handling procedures are necessary. Moisture is detrimental to pyrochemical operations, and the necessary operating temperature (800°C) for the pyroredox oxidation step is above the boiling point of ZnCl_2 (732°C). For these reasons, we mixed the ZnCl_2 with KCl to form a eutectic composition ($\text{KCl} \cdot 45.1 \text{ wt\% ZnCl}_2$), which is much less hygroscopic than pure ZnCl_2 and is stable at temperatures >800°C.

Preparation of this salt was complicated by its high affinity for water and the large volume needed for process demonstration. The established procedure was to sparge a batch of the predried molten salt mixture

*Vacuum-transfer will be discussed in more detail in the sections describing fused pyroredox and fused CaCl_2 production.

TABLE II. Impurity Levels in Fused MSE Salt Mixtures

| Impurity ^a | NaCl · KCl · MgCl ₂ ^b (ppm or wt%) | CaCl ₂ · KCl · MgCl ₂ ^c (ppm or wt%) |
|---------------------------|---|--|
| Alkalinity | 0.23 wt% | 0.24 wt% |
| Ag | <1 | <1 |
| Al | 9 | 14 |
| B | 4 | 8 |
| Ba | 6 | 3 |
| Be | <1 | <1 |
| Bi | <3 | <10 |
| Ca | 300 | Major |
| Cd | <10 | <10 |
| Ce | <30 | <30 |
| CO ₃ | <10 | <10 |
| Co | <3 | <3 |
| Cr | <3 | <3 |
| Cu | <1 | <1 |
| Fe | 14 | 14 |
| Ga | <3 | <3 |
| H ₂ O | 0.22 wt% | 0.21 wt% |
| Hf | <300 | <120 |
| K | Major | Major |
| La | <10 | <10 |
| Li | <3 | <50 |
| Mg | Major | Major |
| Mn | <3 | <1 |
| Mo | <3 | <10 |
| Na | Major | 565 |
| Nb | <30 | <30 |
| Ni | 11 | <10 |
| Total oxygen ^d | 0.22 wt% | 0.25 wt% |
| Pb | <10 | <10 |
| Pt | <30 | <10 |
| Rb | <100 | <80 |
| Re | <30 | <30 |
| Si | <30 | <30 |
| Sn | <10 | <10 |
| Sr | <5 | 0.1 to 1.0 wt% |
| Ta | <300 | <300 |
| Ti | <10 | <10 |
| V | <3 | <3 |
| W | <100 | <100 |
| Y | <3 | <3 |
| Zn | <30 | <100 |
| Zr | <10 | <10 |

^aElements by emission spectroscopy, compounds by wet chemistry, H₂O by drying to constant weight.

^b27.2 wt% NaCl · 34.8 wt% KCl · 38.0 wt% MgCl₂.

^c22.3 wt% CaCl₂ · 45 wt% KCl · 32.7 wt% MgCl₂.

^dTotal oxygen by neutron activation.

with anhydrous HCl for 4 to 5 h and then vacuum-filter the melt into a sacrificial pyrex assembly that was later broken away to recover the salt (Fig. 2). This procedure was time-consuming and required many furnace runs per week to meet the demand. We conducted experiments to reduce the gas contact time and to increase the production per furnace run.

The HCl conditioning and filtration removed water and impurities and converted metallic oxides to chlorides. When melted, the $ZnCl_2 \cdot KCl$ mixture is opaque, viscous, and does not readily filter. The addition of HCl to the melt improves the color and viscosity, allowing filtration. We suspect certain hydrolysis reactions are reversed during the conditioning and that metallic chlorides are formed, precipitated, and removed by filtration. Table III lists impurity levels in filtered product salts; Fig. 3 is a photograph of the filter cake collected after a production run.

Our first experimental objective was to minimize the 4- to 5-h gas contact time. Figure 4 illustrates that total oxygen and water content of the salt varies only slightly (0.08 wt% to about 0.05 wt%) after 3 h of HCl contact. This decrease did not appear to justify a full 5-h gas contact time.

All off gas from the fusing operation is routed through caustic scrubbers for HCl neutralization before venting to the atmosphere. For several runs, we monitored the pH of the lead scrubber (Fig. 5) and compared these profiles with profiles generated from straight neutralization of scrubber solution with HCl (Fig. 6). The profiles fall into the same region after approximately 2 h, in-

dicating HCl consumption is complete early in the process and 5 h of HCl treatment is excessive. These data and the data shown in Fig. 4 indicated that a reduction in HCl contact time would not affect product salt quality.

In conjunction with reducing contact time, we were also interested in increasing salt production by removing the molten salt from the vessel after HCl conditioning. Removing the salt would allow us to add fresh salt to an already preheated vessel. We accomplished this by vacuum-transferring the salt from the hot vessel to an ambient-temperature mold where it could cool under argon. Figure 7 illustrates the two transfer techniques we considered: pressure-assist and vacuum-assist. We chose vacuum-transfer because of its inherent safety. A leak in a pressurized system may spray salt or rupture a vessel; if a leak develops during vacuum-transfer, vacuum is lost and no movement of salt occurs.

The semicontinuous vacuum-transfer apparatus we developed (Figs. 8 and 9) replaced the original system shown in Fig. 2. The new system provides HCl conditioning and filtration, as well as vacuum-transfer and chill-casting of the salt product. The new system triples the salt production of the original batch process without affecting salt quality. Unlike the batch apparatus of Fig. 2, the new system components are reusable. The only major change is the use of a coarse-porosity filter rather than medium-porosity filter. This change keeps the liquid velocity sufficiently high in the transfer tube to minimize plugging. If plugging does occur, the binary salt is readily soluble in water, enabling easy cleaning.

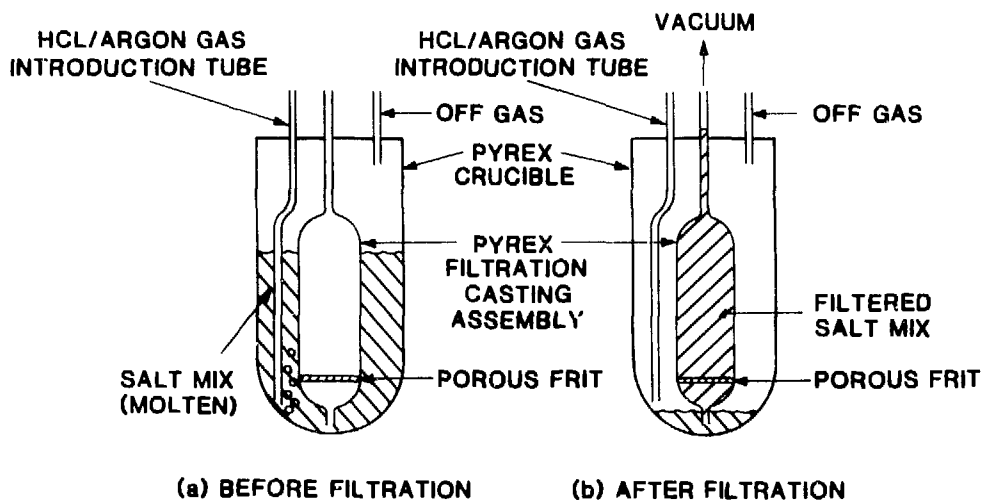


Fig. 2. Batch pyroreodox salt production apparatus.

TABLE II. Effect of Filtration on Impurity Levels in Pyroredox Feed Salts

| Impurity ^a | Unfiltered (ppm or wt%) | Filtered (ppm or wt%) | Filter Cake (ppm or wt%) |
|---------------------------|----------------------------|--------------------------|-----------------------------|
| Ag | <1 | <5 | <1 |
| Al | <20 | <20 | 800-1000 |
| B | <10 | <10 | 50-60 |
| Ba | <30 | <30 | 25-100 |
| Be | <2 | <2 | <1 |
| Bi | <5 | <10 | <10 |
| CO ₂ | <10 | <10 | <10 |
| Ca | 100 | <100 | 200-300 |
| Cd | <5 | <10 | <10 |
| Ce | <10 | <10 | <10 |
| Co | <5 | <3 | <3 |
| Cr | <5 | <5 | 4-25 |
| Cs | <100 | <100 | <100 |
| Cu | <5 | 1-2 | <1 |
| Fe | <20 | <25 | <20 |
| H ₂ O | 0.2 wt% | 0.1 wt% | 0.1 wt% |
| Hf | <150 | <100 | <100 |
| La | <15 | <10 | <10 |
| Li | <5 | <5 | <5 |
| Mg | <10 | <25 | 30-200 |
| Mn | <3 | <3 | 6 |
| Mo | <5 | <3 | <3 |
| Na | <15 | <15 | 70-100 |
| Nb | <30 | <30 | <30 |
| Ni | <5 | <3 | <3 |
| Total oxygen ^b | 0.06 wt% | 0.06 wt% | - |
| Pb | <7 | <3 | <3 |
| Rb | <75 | <50 | <100 |
| Re | <15 | <30 | <30 |
| Se | <60 | <60 | <60 |
| Si | <15 | <20 | 1000-1500 |
| Sn | <5 | <5 | <5 |
| Sr | <5 | 1-2 | <2 |
| Ta | <150 | <100 | <100 |
| Ti | <5 | <5 | <3 |
| V | <5 | <3 | <3 |
| W | <150 | <100 | <100 |
| Y | <5 | <3 | <3 |
| Zr | <15 | <10 | <10 |

^aElements by emission spectroscopy, compounds by wet chemistry, H₂O by drying to constant weight.

^bTotal oxygen by neutron activation.

reactions of the form $\text{CaCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + 2\text{HCl}$. After drying, we split the salt into 5-kg increments, then sealed them by double-bagging in polyvinylchloride bags. This bagged salt was then sent to another Los Alamos facility for isostatic pressing into cylinders. The pressing provided volume reduction, which eased handling, minimized surface area, and provided the correct shape for loading into DOR. After pressing, we removed the plastic bags and stored the salts in vacuum ovens until needed.

This procedure was successful from a DOR processing standpoint but had disadvantages. Among them was the potential for carbon contamination from the plasticizer in the plastic bags. Figure 10 shows photographs of typical pressed salts just before use in DOR. The black surface contamination is thought to be carbon, which cannot be determined in CaCl_2 by current analytical techniques. Carbon is difficult to remove from plutonium by pyrochemistry because low carbon concentrations form high-melting plutonium carbide.

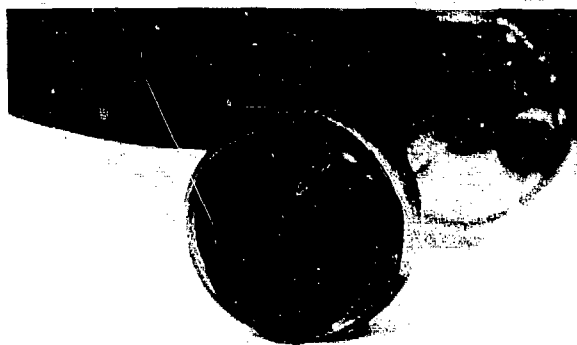


Fig. 3. Filter apparatus with filter cake from pyroredox salt production.

D. Direct Oxide Reduction Salt

The DOR processing step and the other residue treatment operations use CaCl_2 as a diluent or a solvent salt. The demand for this common salt far exceeds other salts. Before 1984, we prepared CaCl_2 by drying the as-received salt (Mallinckrodt or Americium International Chemical food-grade) in a vacuum oven for 5 to 7 days at 100°C, followed by 5 to 7 days at 225°C. This drying was necessary to remove absorbed moisture from the hygroscopic salt and to prevent unwanted hydrolysis

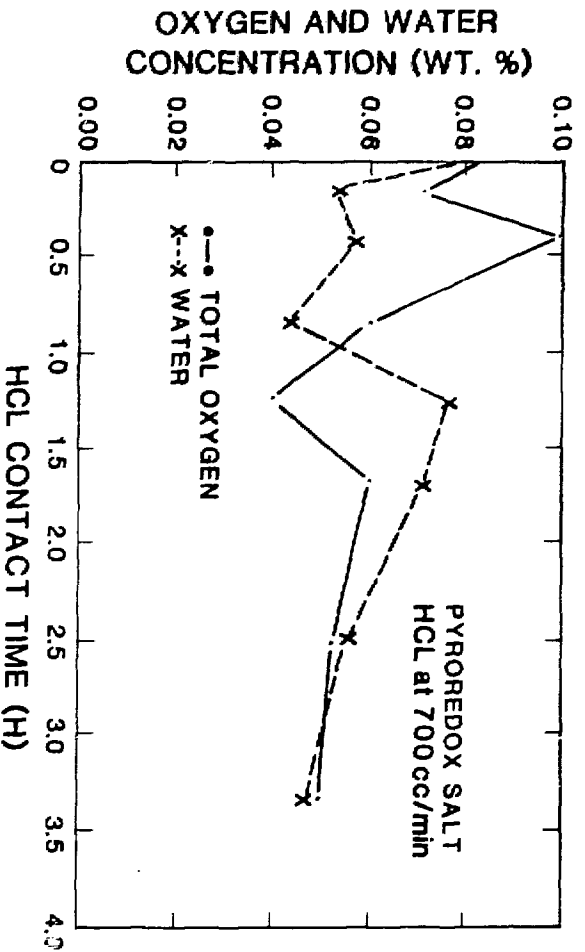


Fig. 4. Total oxygen and water in pyroreodox salt as a function of HCl gas contact time.

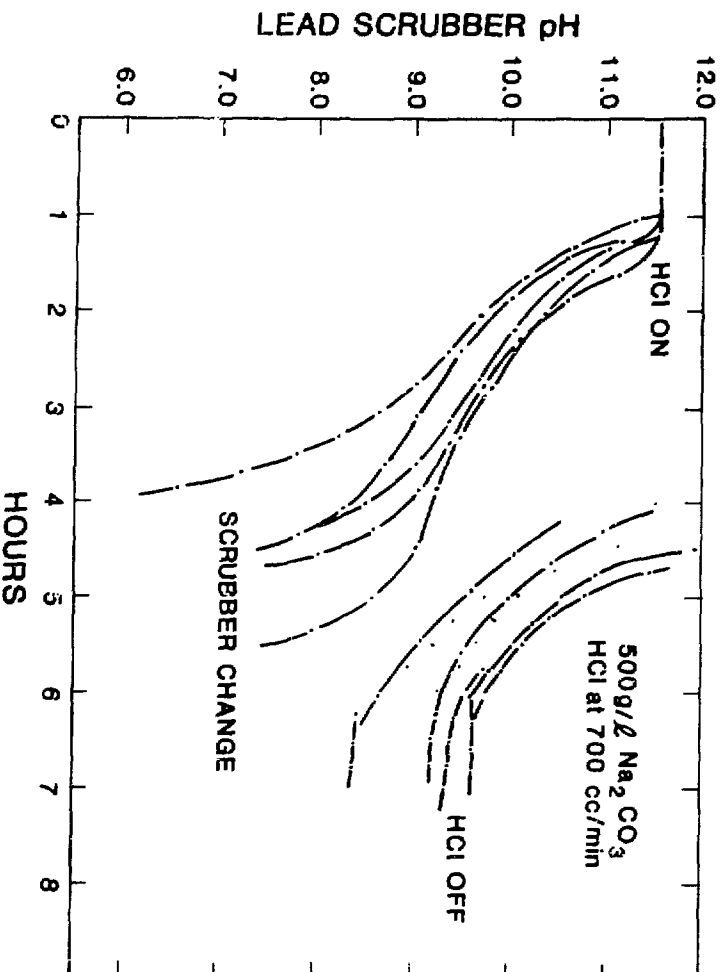


Fig. 5. Neutralization of scrubber solution during pyroreodox salt preparation.

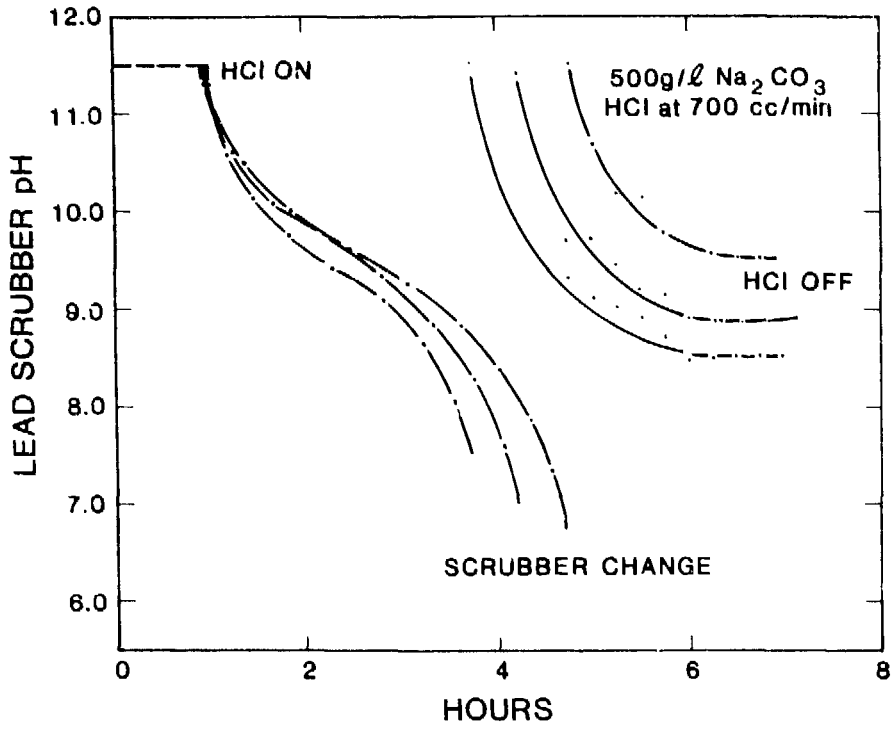


Fig. 6. Neutralization of scrubber solution with anhydrous HCl.

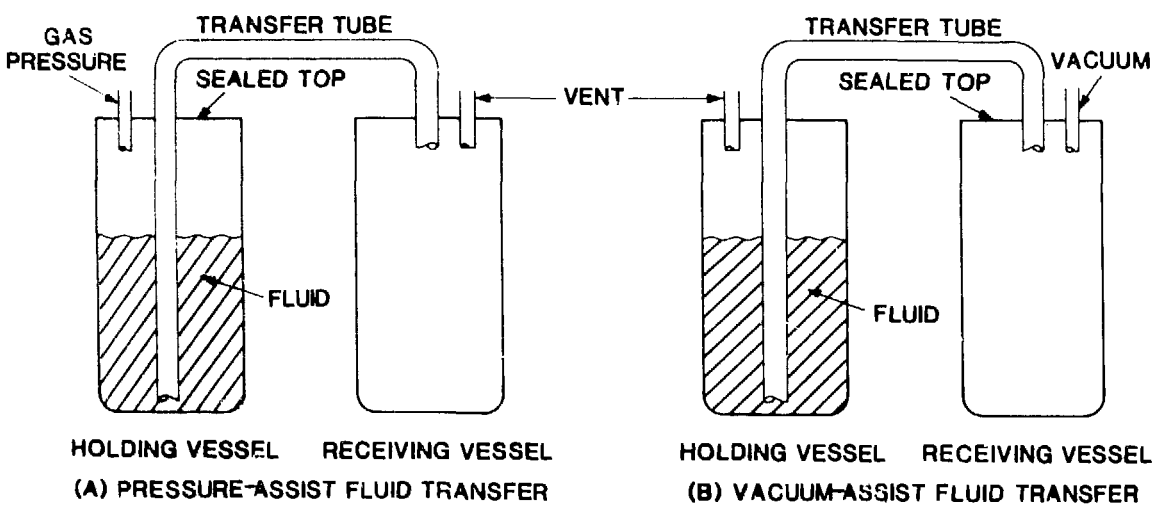


Fig. 7. Schematic of pressure-assist and vacuum-assist fluid transfer.

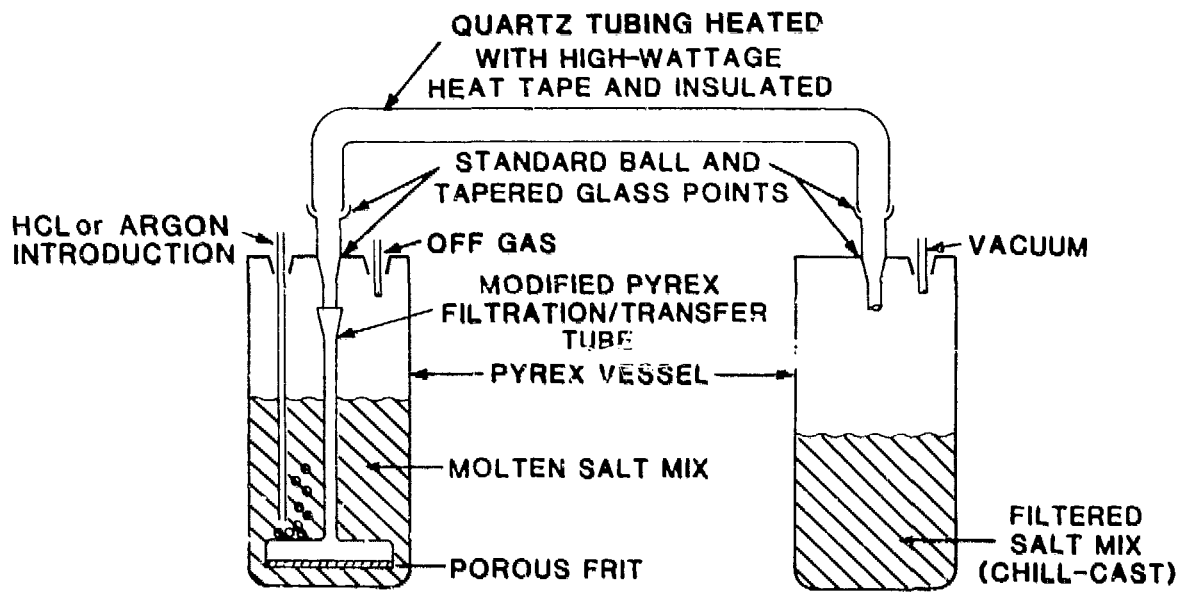


Fig. 8. Apparatus used in semicontinuous pyroredox salt preparation.

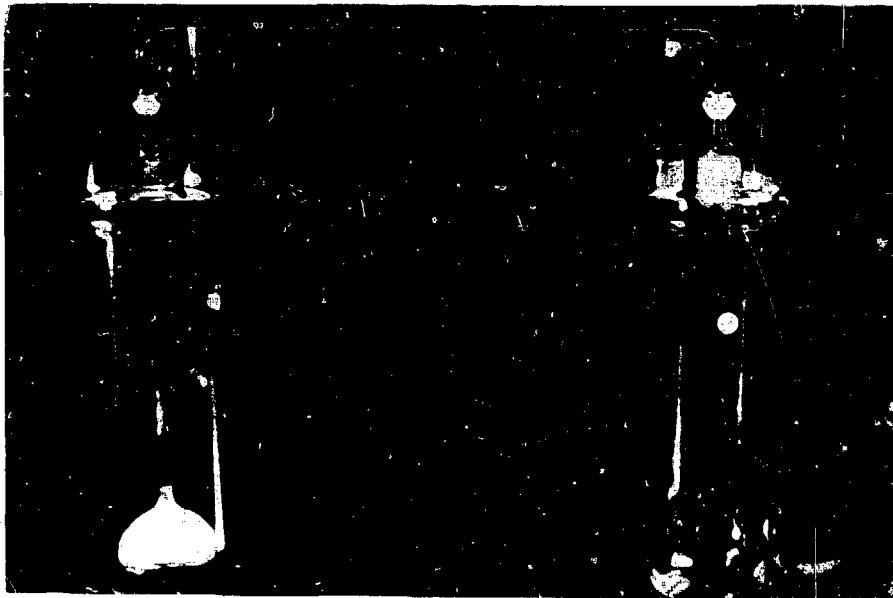


Fig. 9. Production apparatus for use in continuous filtering, transferring, and casting pyroredox salts.



Fig. 10. Pressed CaCl_2 before use in DOR showing probable carbon contamination from plasticizer.

We wanted to improve processing economics and product availability by performing CaCl_2 preparation in-house. In-house preparation would allow us to minimize the carbon and total oxygen content of the salt (total oxygen is determined by neutron activation and includes all oxy-species in the salt). In the DOR reaction, calcium metal is consumed by oxy-species and forms CaO , which could oversaturate the solvent. Oversaturation hinders plutonium metal coalescence due to salt density and viscosity increases, which reduce process yields.

We found that by fusing and casting the CaCl_2 , we could better control the geometry, further minimize the surface area for moisture absorption, eliminate carbon contamination from plasticizers, better respond to changes in salt demand, and also provide some pretreatment to the salt for the removal of water and oxy-species.

Since we had developed vacuum-transfer for the production of pyroredox salts, it was logical to apply the technique to the production of fused CaCl_2 . Because CaCl_2 expands as it freezes, we cast the salt into split molds. Originally, the cylindrical molds were constructed from 316 stainless steel with 3/8- to 1/2-inch-thick walls, coated with either erbia or yttria to passivate the steel surface. This preparation was normally good for 50 to 75 castings before the metal began to show. We now use aluminum molds (alloy 6061) with 1/2-inch-thick walls. Aluminum molds are lighter, cheaper,

provide better heat transfer characteristics, do not contaminate the salt, and have a lifetime of about 200 castings. We are currently evaluating various grades and thicknesses to determine the best mold material.

The procedure for fusing CaCl_2 consists of three operations: melting and conditioning in platinum, vacuum-transferring through either platinum or tantalum, and casting into aluminum split molds. Currently, fused CaCl_2 is prepared as follows: 5.5 kg of undried CaCl_2 are fed into a platinum crucible in a furnace preheated to 350°C. Argon gas is flushed over the salt as it melts. Once the salt is molten, HCl is sparged into the salt for ~30 minutes to dehydrate the salt and convert oxide impurities to chlorides. The salt is then sparged with argon to purge the system of HCl , vacuum-transferred through a heated 1/2-inch-o.d. platinum tube, and cast in split aluminum molds. The off gas line from this system is kept free of condensed water and all off gas is routed through caustic scrubbers for neutralization prior to venting to the atmosphere. The total preparation time from loading the loose salt into the furnace to casting the molten salt is approximately one hour.

Table IV shows that fused and cast salt has equivalent quality to pressed salt. Figures 11 and 12 show typical fused salts ready for use. To date, most of our efforts have involved comparing the performance of fused and pressed CaCl_2 in the DOR process. We collected the data in Table V from 57 difference batches of foundry-grade PuO_2 .

TABLE IV. Semi-Quantitative Analyses for Fused and Pressed CaCl₂

| Impurity | Pressed CaCl ₂ (ppm or wt%) | Fused CaCl ₂ (ppm or wt%) |
|------------------|---|---|
| CaO | 0.10 wt% | 0.09 wt% |
| H ₂ O | 0.3 wt% | 0.3 wt% |
| Al | <60 | <80 |
| B | 5-100 | 3-100 |
| Ba | <5 | <10 |
| Be | <1 | <1 |
| Bi | <4 | <4 |
| CO ₂ | <10 | <10 |
| Cd | <4 | <4 |
| Ce | <100 | <100 |
| Co | <4 | <4 |
| Cr | <4 | <4 |
| Cu | <10 | <10 |
| Er | <40 | <40 |
| Ga | <100 | <100 |
| Ge | <4 | <4 |
| Hf | <120 | <100 |
| In | <4 | <4 |
| K | 600-25000 | 600-25000 |
| La | <10 | <10 |
| Li | <300 | <500 |
| Mg | <500 | <500 |
| Mn | <1 | <1 |
| Mo | <4 | <10 |
| Na | 60-8500 | 60-8500 |
| Nb | <4 | <10 |
| Ni | <4 | <10 |
| Total oxygen | 0.55 wt% | 0.45 wt% |
| P | <120 | <120 |
| Pb | <4 | <4 |
| Pt | - | <10 |
| Rb | <300 | <120 |
| Re | <40 | <40 |
| Si | <100 | <250 |
| Sn | <4 | <4 |
| Sr | 100-10000 | 100-10000 |
| Ta | <100 | <100 |
| Ti | <4 | <4 |
| V | <4 | <4 |
| W | <360 | <100 |
| Y | <4 | <4 |
| Zn | <60 | <100 |
| Zr | <12 | <12 |

The data in Table V indicate that fused CaCl₂ performs at least as well as pressed salt in overall process recoveries and may reduce rerun frequency. These data helped justify converting from pressed CaCl₂ to fused

CaCl₂ in our pyrochemical operations. We had been using predried CaCl₂ (scheduled for pressing) as feed for fusing, but planned facilities upgrades have shut down our drying furnaces for an extended time. Because of this shutdown, we have had to fuse undried or as-received CaCl₂. Table VI compares DOR performance of fused, undried CaCl₂ and fused, predried CaCl₂.

These data indicate that with proper preparation, undried CaCl₂ may be fused directly, without compromising either its quality or performance in DOR.

We are continuing to develop the fusing and casting procedure. Efforts in the area of CaCl₂ conditioning include determining the minimum amount of HCl necessary to produce a salt with an acceptable total oxygen content (<0.4 wt%). Tests have included flushing HCl gas over the surface of the salt, HCl sparging in the salt, and using an argon flush or sparge only. Results indicate that any of these procedures produces acceptable salts.

Figure 13 is a schematic of our transfer tube construction and Fig. 14 is a photograph of an actual device. We are wrapping the tubes with commercially available high-wattage heat tape with operating temperatures around 850°C. These tapes are not compatible with metal surfaces nor can the tape overlap itself without developing an electrical short. We eliminate these problems by using a ceramic isolation sleeve to prevent tape contact with the metal tubing and by wrapping the tape carefully. These precautions and good insulation are necessary to heat the region of the transfer tube between the hot furnace and the casting mold to over 800°C.

IV. ACKNOWLEDGMENTS

All solvent salt production, most process and equipment development, optimization, and new concept implementation occur in a nonradioactive facility, which also serves as a training ground for MST-13 employees, providing glovebox, R&D, production, and troubleshooting experience.

Individuals who helped develop the facility over the past three years include J. A. McNeese, S. A. Apgar, P. C. Lopez, W. K. Drennon, D. A. Hutchins, M. J. Chavez, D. W. Anderson, J. J. Lovato, J. J. Simpson, R. E. Mascarenas, M. D. Ferran, E. D. McCormick, J. Y. Coulter, C. E. C. Rense, and F. A. Stephens. University summer students who have contributed include A. E. Buchholtz, K. J. Partin, L. A. Brockway, M. M. Moy, J. C. Kammer, and A. J. Figel. We would also like to acknowledge our analytical chemistry group (CHM-1), whose personnel performed thousands of analyses on hundreds of samples. Without their timely response, the salt production and handling techniques we use today would still be in development.



Fig. 11. Fused CaCl_2 in an aluminum split mold.



Fig. 12. Fused CaCl_2 ready for packaging in an inert glovebox.

TABLE V. Comparison of Pressed CaCl_2 and Fused CaCl_2 in DOR

| Salt Type | DOR Runs | Rerun Frequency* (%) | Overall Pu Recovery (%) |
|-----------|----------|----------------------|-------------------------|
| Pressed | 397 | 20 | 93.7 |
| Fused | 477 | 11 | 94.4 |

*A rerun occurs through equipment failure or through unacceptable metal recoveries.

TABLE VI. Comparison of Undried and Predried Fused Salts in DOR

| Salt Type | Total Oxygen (wt%) | DOR Runs | Rerun Frequency (%) | Overall Pu Recovery (%) |
|-----------------|--------------------|----------|---------------------|-------------------------|
| Undried, fused | 0.34 | 121 | 11.6 | 94.3 |
| Predried, fused | 0.34 | 356 | 11.0 | 94.5 |

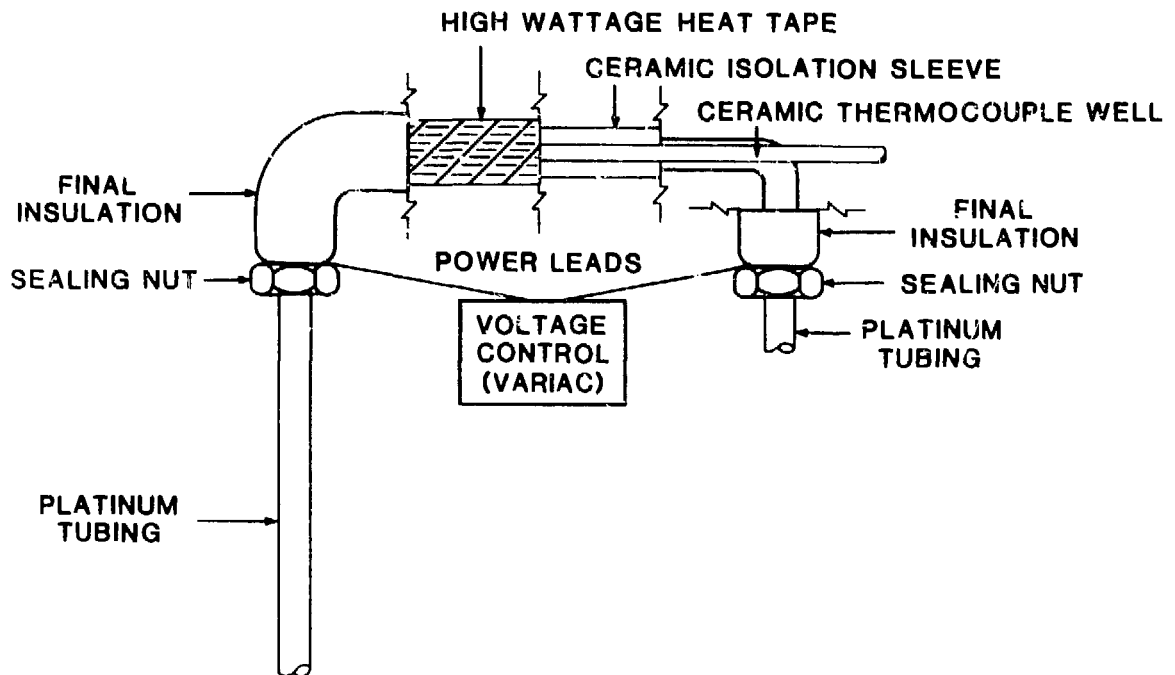


Fig. 13. Schematic of transfer tube for vacuum-transfer of molten salt.

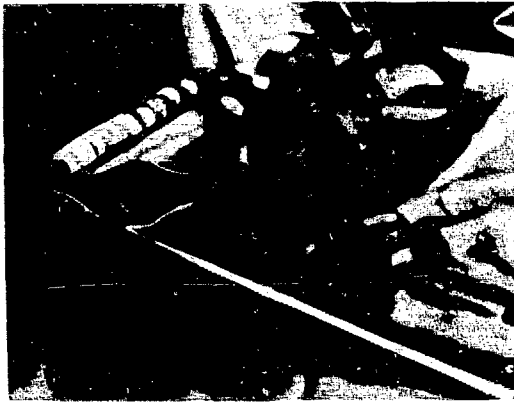


Fig. 14. Platinum transfer tube for casting CaCl_2 . The tube is shown with an attachment used to seal against the split mold.

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