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TITLE: RECENT DEVELOPMENT IN PYROCHEMISTRY AT LOS ALAMOS

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RECENT DEVELOPMENTS IN PYROCHEMISTRY AT LOS ALAMOS

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ABSTRACT

Recent developments in pyrochemical processing at Los Alamos include the recovery of plutonium from anodes and impure metal by pyroredox and new molten salt handling and purification techniques. The anode is dissolved in a $ZnCl_2$-KCl salt to form $PuCl_3$ and a zinc and impurities button. Calcium reduction of the $PuCl_3$ yields 95-98% pure plutonium. New techniques for transferring molten salt from a purification or regeneration vessel to molds has been successfully developed and demonstrated. Additional salt work involving recycle of direct oxide reduction salts using anhydrous hydrogen chloride, phosgene, and chlorine gases is under way.

DISCLAIMER

The general pyrochemical processing scheme for metal production and residue recycle is shown in Figure 1. Major efforts in R&D have involved the recovery of plutonium from impure metal and molten salt handling and recycle. These new developments will be examined in detail.

The recovery of plutonium from impure metal has historically been accomplished by burning the metal to oxide and separating the impurities by aqueous processes. Los Alamos National Laboratory has developed and is productionizing a pyrochemical method of recovering plutonium from impure metals.

The process, pyroredox, is based on the differences in the free energies of formation of various metal chlorides with respect to $ZnCl_2$. Table 1 is a tabulation of metallic chloride free energies at 1000°K.* All the metals having chlorides with more negative free energies than $ZnCl_2$ will reduce the $ZnCl_2$ to metallic zinc, while all the metals having chlorides with a less negative free energy of formation will not reduce $ZnCl_2$ and will remain metallic.

The pyroredox process is currently being used to recycle spent anodes from the electrorefining process. Figure 2 is a block diagram of the steps in this anode recovery process. The feed is an anode from a completed electrorefining run. These anodes are generated when the electrorefining process shuts down due to anode solidification or high back EMF within the electrorefining cell. In either case the impurity level in the anode is too high for further processing in electrorefining. The plutonium content of the anode is typically 88-90% by weight. The remainder of the anode is metal impurities, principally gallium.

The first step is a polishing process, Figure 3, using Ca to reduce any oxides to metal. Oxides may be generated during handling by exposure to the dry air glovebox atmosphere. Most often, however, anodes have a delay in processing while being calorimetered. This may take from one day to two weeks depending on NDA equipment availability. A thin layer of oxide will accumulate during this wait and must be reduced to metal prior to further processing. This step also helps clean the anode of any adhering salts or salt inclusion from electrorefining.

After polishing, the anode is reacted with a molten 31 mole % $ZnCl_2$-KCl eutectic salt. This salt composition was chosen because of the ease of preparation and because it is close to the compound K_2ZnCl_4. This salt does not pick up moisture after preparation. Figure 4 shows the basic chemistry of the process. The major anode impurities that will reduce $ZnCl_2$ are Am, U and Al. Aluminum chloride, however, is very volatile and will boil off. All remaining impurities such as Ga, Ta, Fe and W remain metallic and combine with the generated zinc to form a metal button. This button is typically discardable.

The salt phase is predominately a green salt and a slight amount of grey salt. X-ray diffraction has shown the green salt to be 90-95% K_2PuCl_6 with the remainder KCl. This is expected because of the KCl rich matrix initially present. The grey phase analyzes 80% K_2PuCl_6, 10% KCl and 10% Zn. The zinc fog tends to increase with decreasing anode purity.

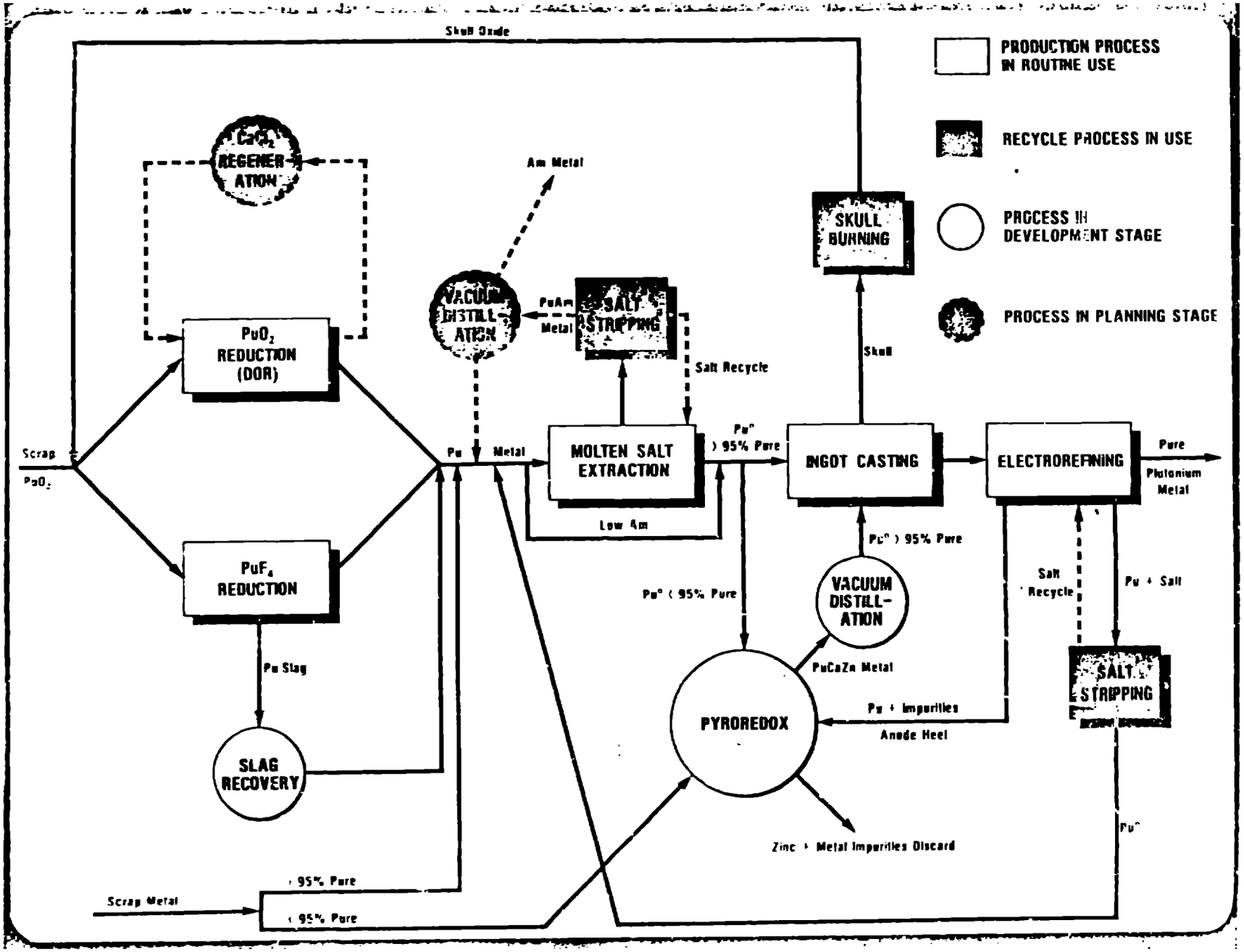
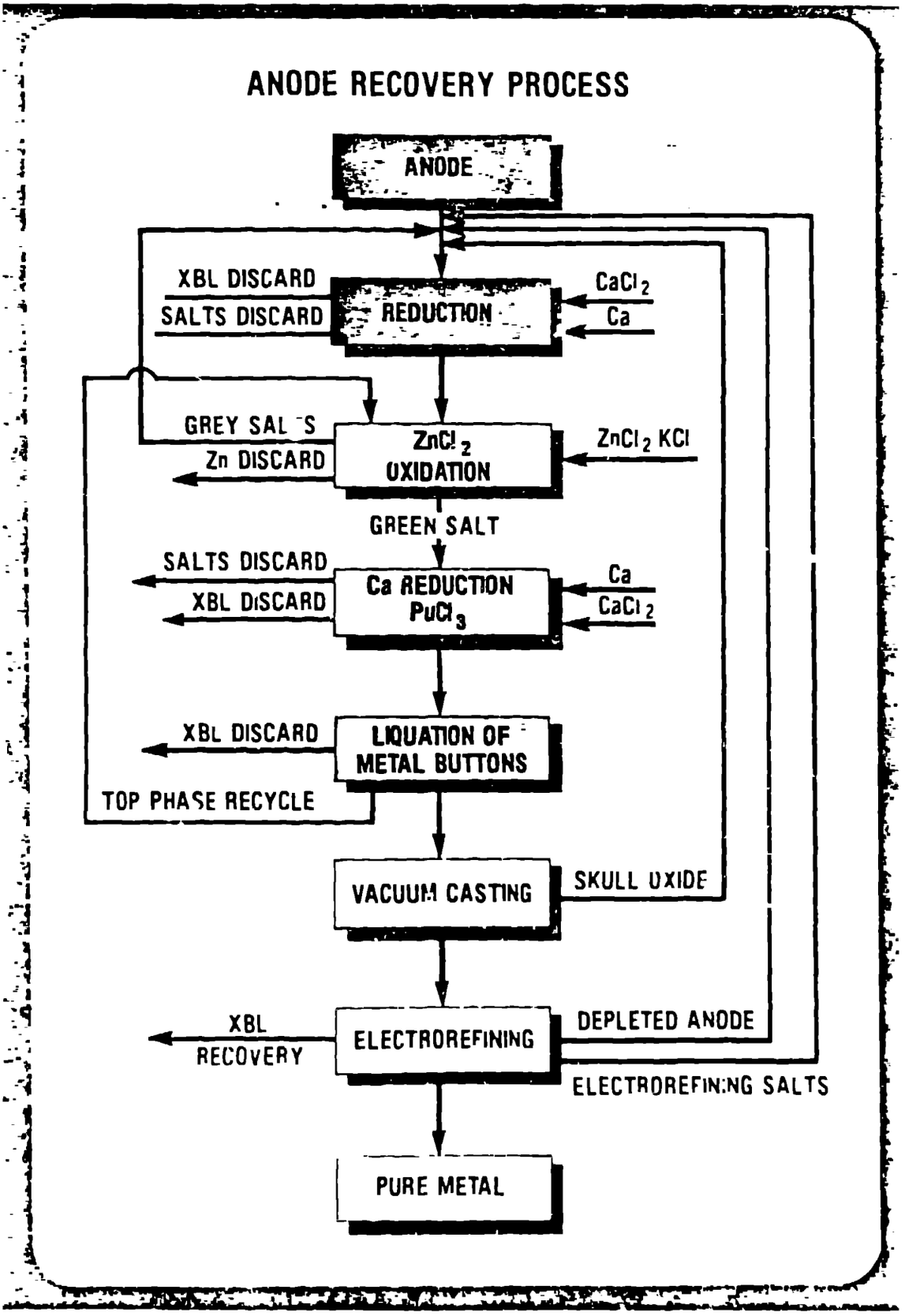

Skull Oxide
PRODUCTION PROCESS IN ROUTINE USE
RECYCLE PROCESS IN USE
PROCESS IN DEVELOPMENT STAGE
PROCESS IN PLANNING STAGE
$CaCl_2$ REGENERATION
Am Metal
SKULL BURNING
VACUUM DISTILLATION
PuAm Metal
SALT STRIPPING
PuO_2 REDUCTION (DOR)
Salt Recycle
Skull
Scrap
PuO_2
Pu
Metal
MOLTEN SALT EXTRACTION
Pu°) 95% Pure
INGOT CASTING
ELECTROREFINING
Pure
Plutonium Metal
Low Am
PuF_4 REDUCTION
Pu°) 95% Pure
Pu° (95% Pure
VACUUM DISTILLATION
Salt Recycle
Pu + Salt
Pu Slag
PuCaZn Metal
SALT STRIPPING
PYROREDOX
Pu + Impurities
Anode Heel
SLAG RECOVERY
Zinc + Metal Impurities Discard
Pu°
) 95% Pure
Scrap Metal
(95% Pure

Table 1

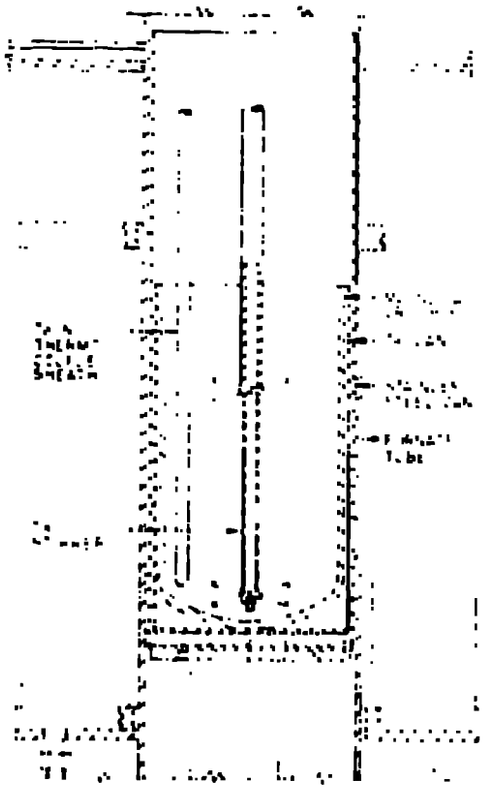
Free Energy of Formation of Chlorides

1000°k

Chloride	-ΔGf (kcal/gr-equiv. Cl)	Reference
KCl	81.6	17
$CaCl_2$	76.7	17
NaCl	76.2	17
$AmCl_3$	67.0	18
$PuCl_3$	58.4	19
$MgCl_2$	57.7	17
UCl_3	54.0	20
$AlCl_3$	47.1	21
$BeCl_2$	42.3	21
$MnCl_2$	42.2	21
$ZnCl_2$	34.1	21
$CrCl_2$	32.8	21
$GaCl_3$	32.5	18
$CdCl_2$	30.4	21
$TaCl_5$	30.4	21
$SiCl_4$	28.0	18
BCl_3	27.4	21
$PbCl_2$	26.5	21
$FeCl_2$	26.3	22
CuCl	22.0	17
$NiCl_2$	18.6	21
WCl_5	6.0	21
WCl_4	5.3	21
WCl_2	4.5	21
WCl_6	4.0	21
CCl_4	- 1.7	21


ANODE RECOVERY PROCESS
ANODE
XBL DISCARD
SALTS DISCARD
REDUCTION
$CaCl_2$
Ca
GREY SALTS
Zn DISCARD
$ZnCl_2$ OXIDATION
$ZnCl_2$ KCl
GREEN SALT
SALTS DISCARD
XBL DISCARD
Ca REDUCTION $PuCl_3$
Ca
$CaCl_2$
XBL DISCARD
LIQUATION OF METAL BUTTONS
TOP PHASE RECYCLE
VACUUM CASTING
SKULL OXIDE
XBL RECOVERY
ELECTROREFINING
DEPLETED ANODE
ELECTROREFINING SALTS
PURE METAL

ANODE PRE-POLISHING



REACTION:

$$(Pu \bullet M)^{-A} + Ca^{\circ} \xrightarrow{850\ C} (Pu \bullet M)^{\circ} + CaCl_2 \bullet CaO$$

Figure 3. Anode pre-Polishing

PYROREDOX: $ZnCl_2$ OXIDATION

REACTION:

$$2(Pu - 0.25\ Ga) + 3\ ZnCl_2 \xrightarrow{750^{\circ}C} 2\ PuCl_3 + (3\ Zn - 0.5\ Ga)$$

OXIDATION PRODUCT AND RESIDUE

ZINC METAL RESIDUE WITH GALLIUM AND OTHER METALLIC IMPURITIES

Further analysis has shown areas near the Zn to contain Ca, Fe, Ta, Cr and Ni. This grey phase is separated and recycled through a polishing step.

The green salt is reduced to Pu metal with calcium, Figure 5. Dried $CaCl_2$ is added to help control the reaction rate by diluting the dried, crushed $PuCl_3 \cdot KCl$ salt. The reaction between the $PuCl_3$ and the calcium is so vigorous that the calcium is added as an ingot to lessen the available surface area. The $CaCl_2$ addition has also been found to eliminate black salt formation in the reduction step.

Yields from the reduction are consistently greater than 98%. The product button is typically a two phase metal. The bottom phase is predominately plutonium with only small amounts of Zn and Ca. The top phase is approximately 50-60% plutonium with the remainder Zn and Ca. These phases can be mechanically separated although a more efficient method has been developed. Liquation, or a gravity separation, segregates the button into two easily separable phases. Figure 6 shows the liquation step. The metal is loaded into a long narrow crucible and held molten at 850°C for six hours. The metal, when removed, easily breaks into an upper phase of density 7-9gm/cm^3 and a lower phase of density 14-15.4gm/cm^3. Analyses shows the lower phase to be 95-98% plutonium with the remainder zinc and a very small amount of calcium. The upper phase is typically 30-60% Pu and the remainder zinc and calcium. The lower, denser phase is of adequate purity to be fed back into electrorefining.

The top phase, containing a significant amount of plutonium can be reoxidized using $ZnCl_2$ in KCl. The zinc is removed from the system as zinc metal and the calcium is oxidized to $CaCl_2$ which is inert in the subsequent pyroredox calcium reduction step. This closes all the recovery loops within the process and only discardable residues are generated.

One of the developments that has facilitated the pyroredox process is improved salt handling and purification capabilities. The $ZnCl_2$-KCl eutectic is produced by melting the appropriate amounts of each reagent in a pyrex glass tube such as that shown in Figure 7.

Undesirable oxygen is removed from the mixture by bubbling HCl through the melt. After conditioning with HCl, argon is sparged through the melt to remove all residual HCl. A filtering tube is then lowered into the melt. The filter is a pyrex frit and is used to remove any large unmelted particles or any insoluble products generated in the HCl conditioning.

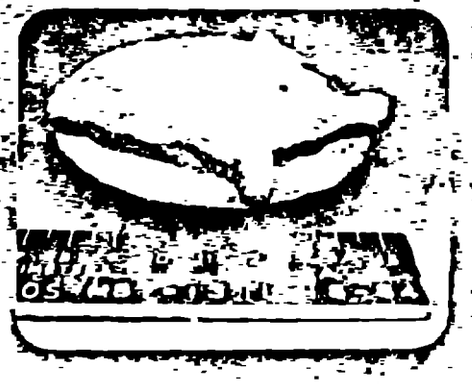
Figure 8 shows the molten salt transfer apparatus for casting the filtered salt into a pyrex mold. All components of this system are quartz or pyrex glass. Because of the length of the transfer tube provisions must be made to maintain the salt in a molten state. Heat tape wrapping such as that shown in Figure 9 serves to keep the transfer tube above the freezing temperature of the salt. The actual movement of the salt results from evacuation of the mold with vacuum or a slight pressurization of the conditioning crucible or both. The $ZnCl_2$-KCl mixture shrinks significantly upon cooling and slips easily out of the mold.

Another major R&D effort is the regeneration of spent direct oxide reduction salts. The $CaCl_2$ salt contains between 7-15 wt. % CaO. The

PYROREDOX: CALCIUM REDUCTION

REACTION:

$$2\,PuCl_3 + 3\,Ca^{\circ} \xrightarrow[800^{\circ}C]{CaCl_2} 3\,CaCl_2 + 2\,Pu$$



REDUCTION PRODUCT AND RESIDUE

2-PHASE METAL PRODUCT

Pyrochemical Reduction

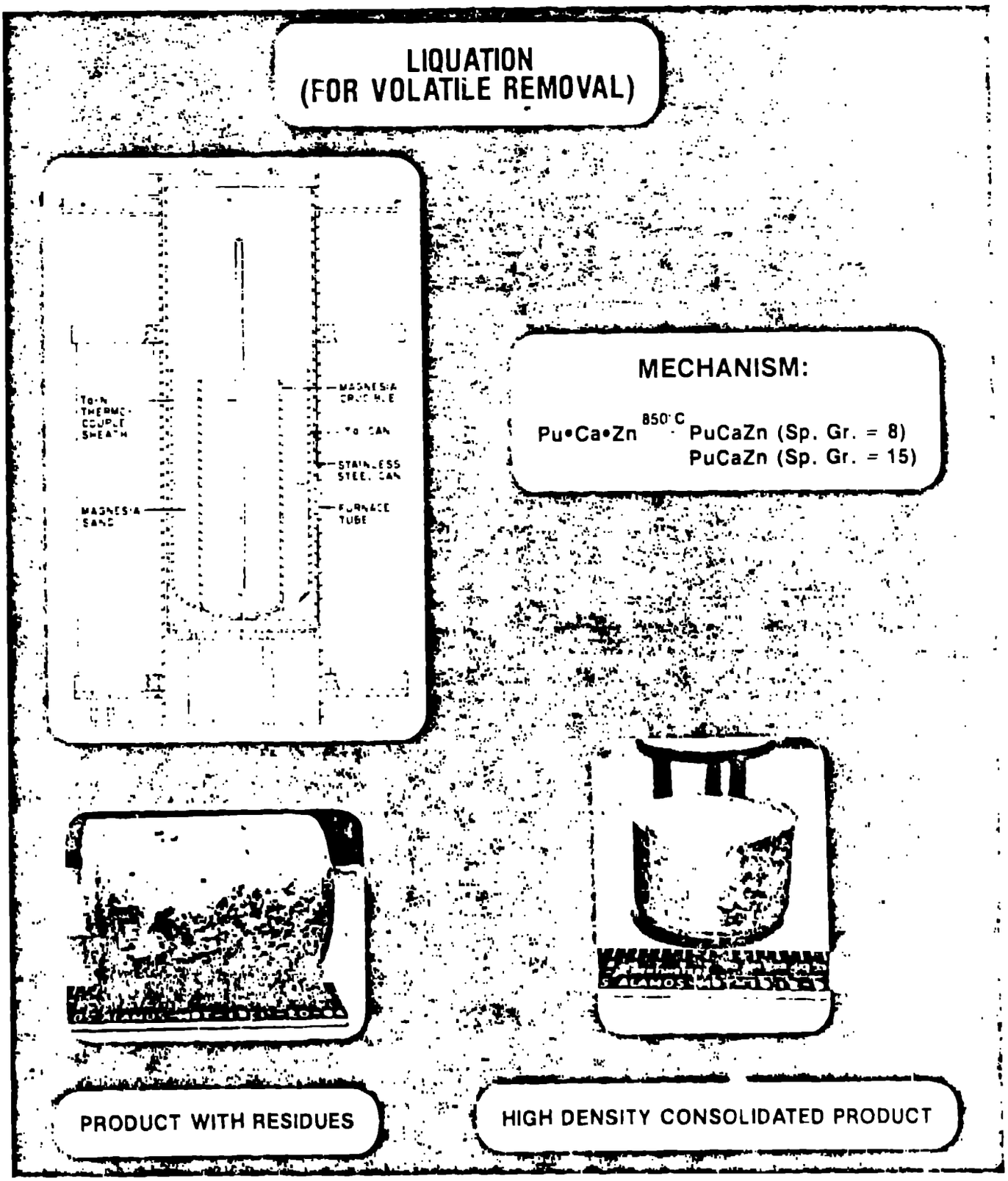


Figure 6. Liquation

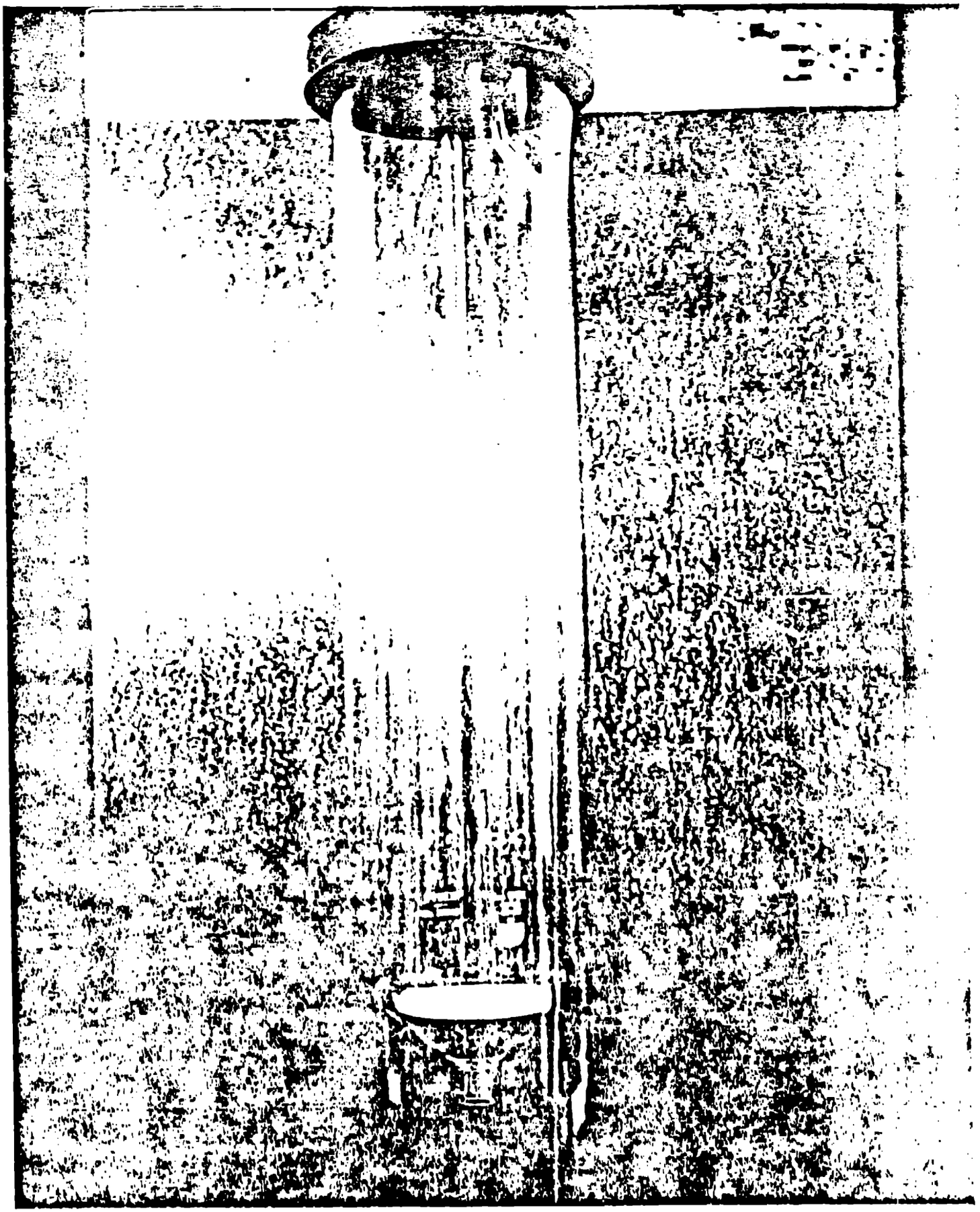


Figure 4 Pyrex Frit

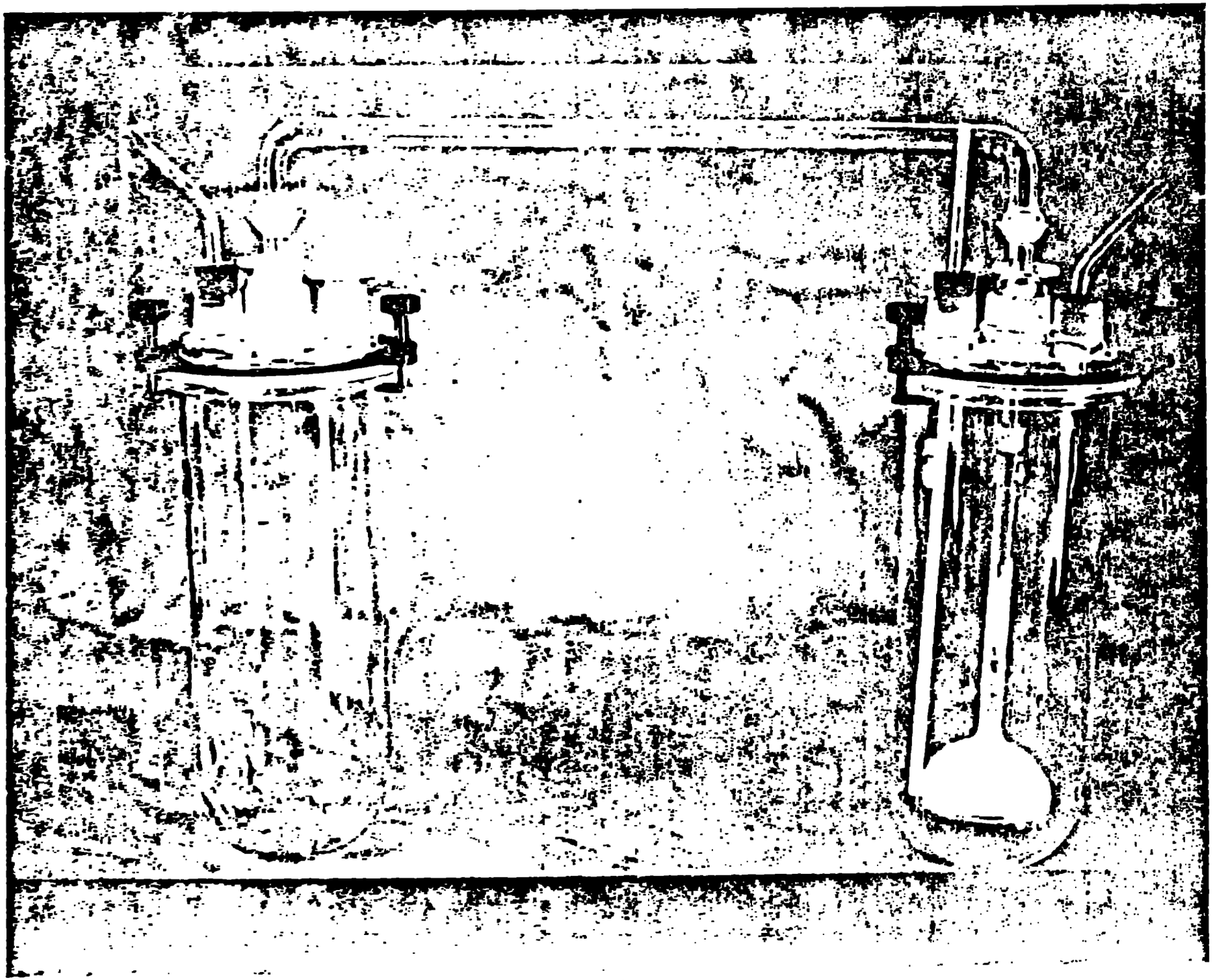


Figure 3. Salt Transfer Apparatus

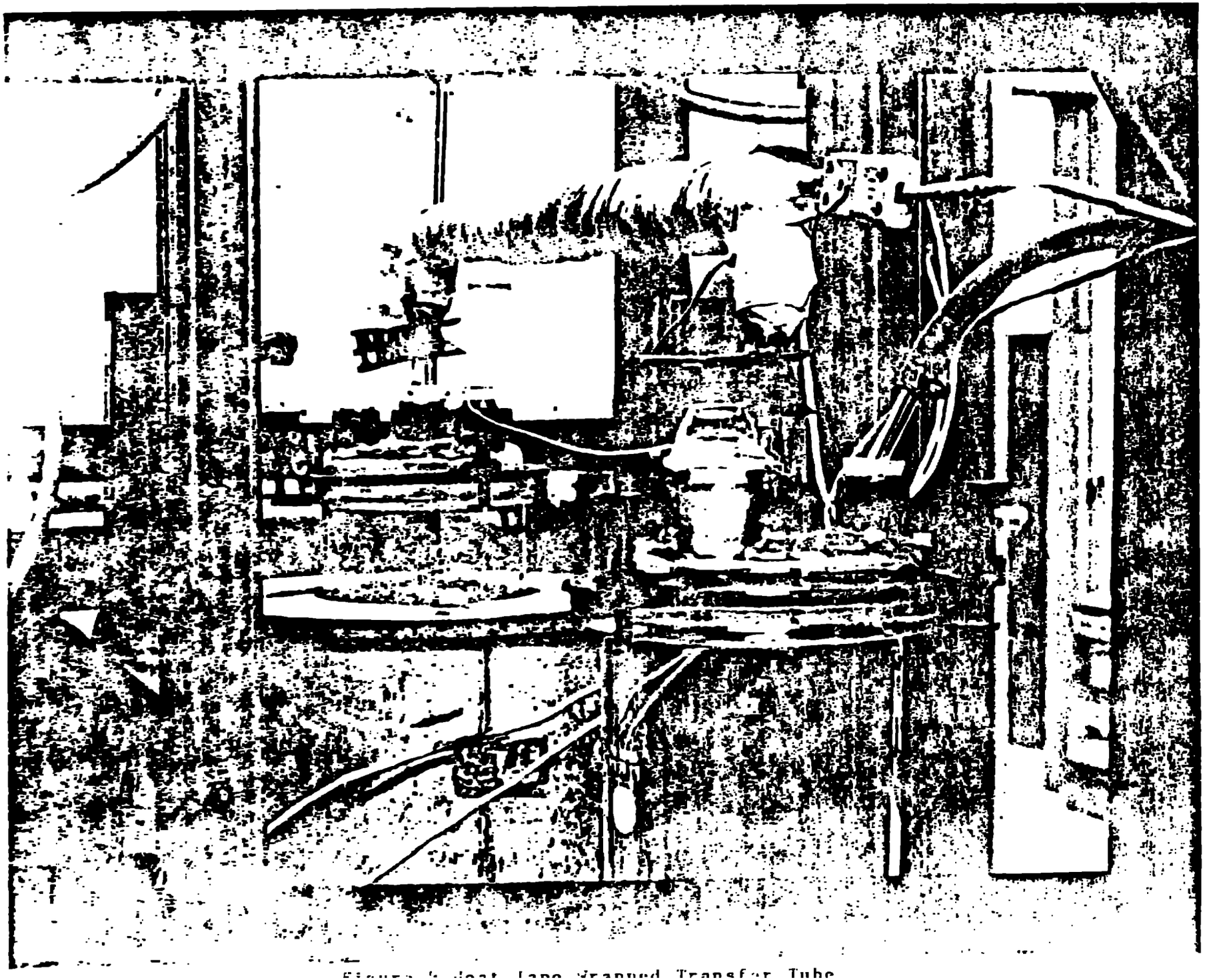


Figure 4. Heat Lamp Wrapped Transfer Tube

calcia is a reaction product from the reduction of plutonium oxide with calcium metal. The salts are good for only a single run because of the relatively low, 18.5%, solubility of CaO in $CaCl_2$ at 850°C. The $CaCl_2$·CaO salt also contains approximately 1 wt. % calcium.

Because the $CaCl_2$·CaO salt is the major residue from the oxide reduction process it is very desirable to close the loop by regeneration of the salt. An additional benefit is the increased purity of the regenerated salt. The calcium added to reduce the PuO_2 also reduces all the impurities in the salt to metals that are then gettered by the extremely active plutonium metal. The resulting salt contains small amounts of uncoalesced plutonium metal, calcia and calcium chloride. The salt is completely free of additional impurities.

Several chlorinating agents have been used in efforts to achieve an acceptable level of CaO removal while not introducing additional oxygen or other impurities. Figure 10 shows the chemistry of this regeneration. The two most promising reagents were initially thought to be anhydrous hydrogen chloride gas and phosgene. The hydrogen from the HCl is a good reducing agent and removes the oxygen in the form of water. Because the regeneration is done in molten $CaCl_2$·CaO, the water will volatilize. This reaction, however is reversible, especially at high temperature.

Phosgene, $COCl_2$ was chosen because the reducing agent, CO, is much stronger than hydrogen and the reaction should be irreversible at high temperature. Phosgene is, however, a very reactive material and very corrosive at high temperature. Platinum was used in the initial tests and tantalum was used in larger scale experiments in the regeneration of spent oxide reduction salts using both HCl and chlorine.

Chlorine was used as a third chlorinating agent because it introduces no other elements into the system. At high temperatures Cl_2 disassociates to provide the atomic chlorine. However because no reducing agent is present the calcia removal was expected to be poor.

Calcia concentration was determined as alkalinity by a wet chemistry method. Figure 11 shows the CaO content as a function of time for the three chlorinating agents. The chlorine appears to be superior to either $COCl_2$ or HCl. The HCl results may be explained by the reversibility of the chlorination reaction. Further study of the $COCl_2$ results led to the possibility of the calcia and carbon dioxide reacting to form calcium carbonate. Carbon analysis on phosgene regenerated samples further support the theory of carbonate formation. As seen in Figure 12 the carbon level of the salt increases dramatically for contact times of up to 60 minutes. The carbon levels begin to fall indicating possible further reaction of the carbonate to form calcium chloride and two molecules of carbon dioxide. From the trend of this data, extremely long contact times would be needed to reduce the carbon levels back to that originally in the salt.

A more specific measure of residual oxygen content is neutron activation. Figure 13 is the oxygen content of regenerated salts as a function of contact times. Again chlorine is clearly the desirable chlorinating agent for removing residual oxygen. Although HCl does remove

- $CaCl_2$ Regeneration and Recycle

$$PuO_2 + 2\ Ca + 11\ CaCl_2 \longrightarrow Pu + 2\ CaO \cdot 11\ CaCl_2$$

1. $CaO + 2\ HCl \longrightarrow CaCl_2 + H_2O$
2. $CaO + COCl_2 \longrightarrow CaCl_2 + CO_2$

(Note: Other chlorinating agents include $MgCl_2$, NH_4Cl, Cl_2)

Figure 10. Calcium Cy...

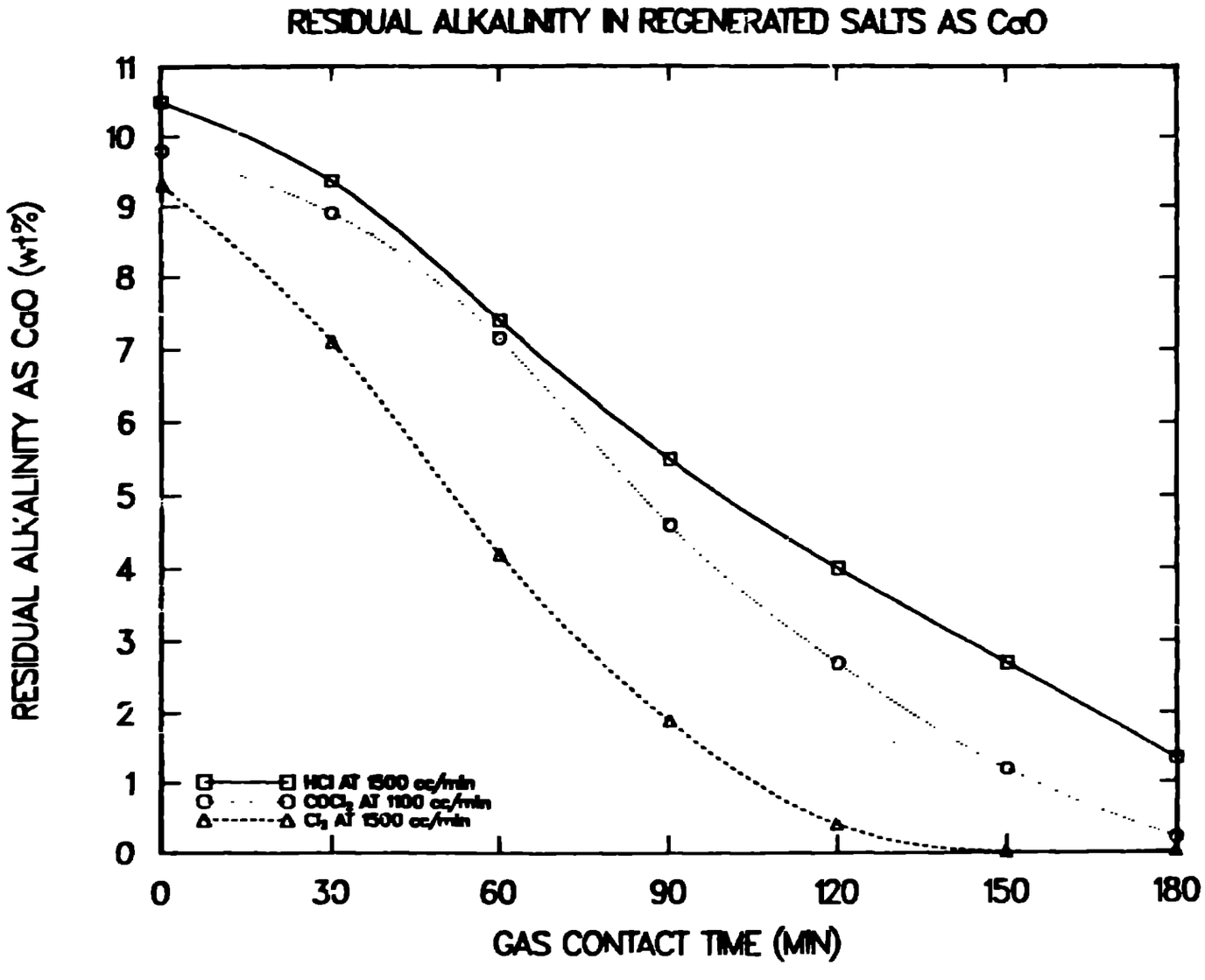


Figure 11. Residual Alkalinity in Regenerated Salts as CaO

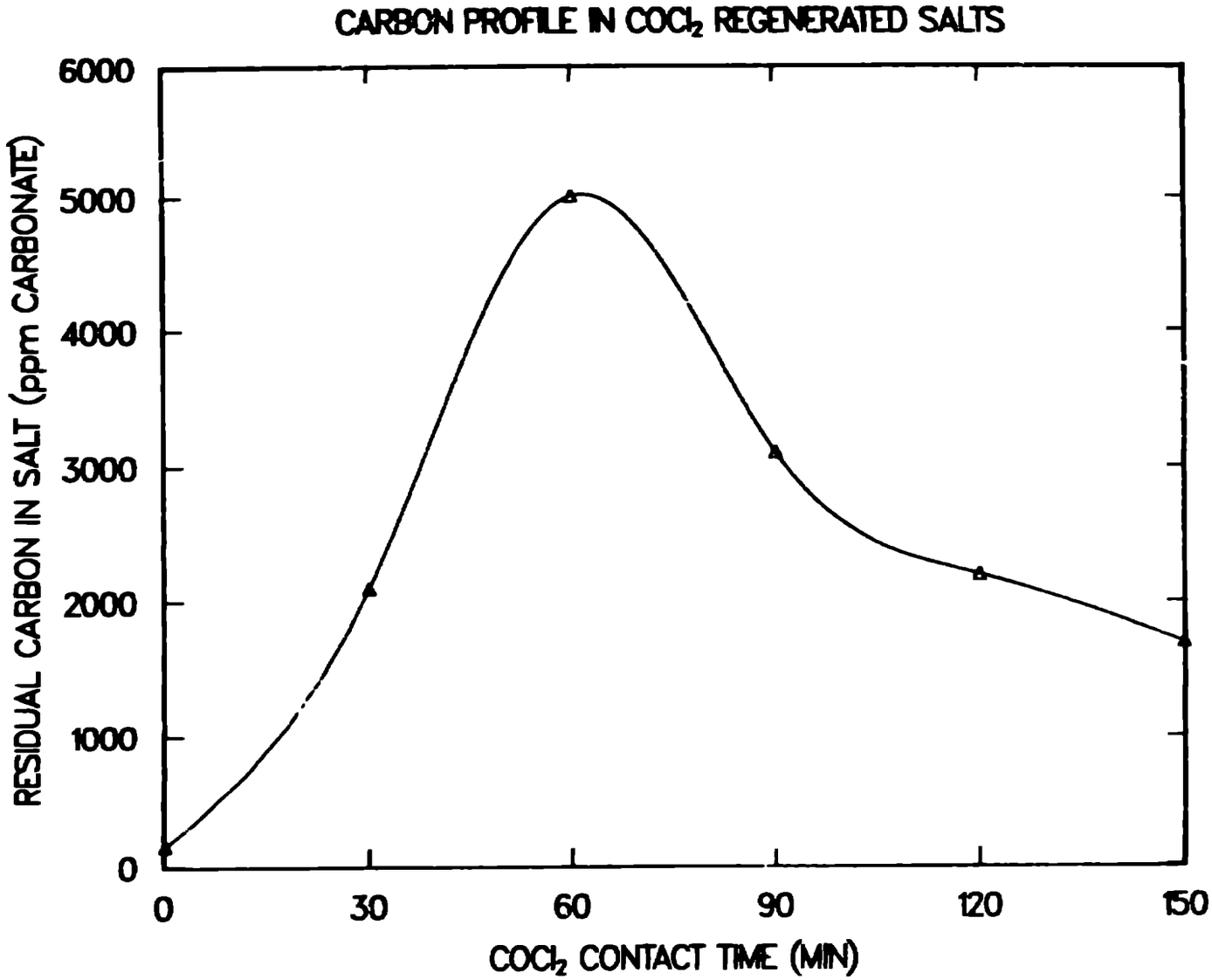


Figure 12. Carbon Profile in $COCl_2$ Regenerated Salts

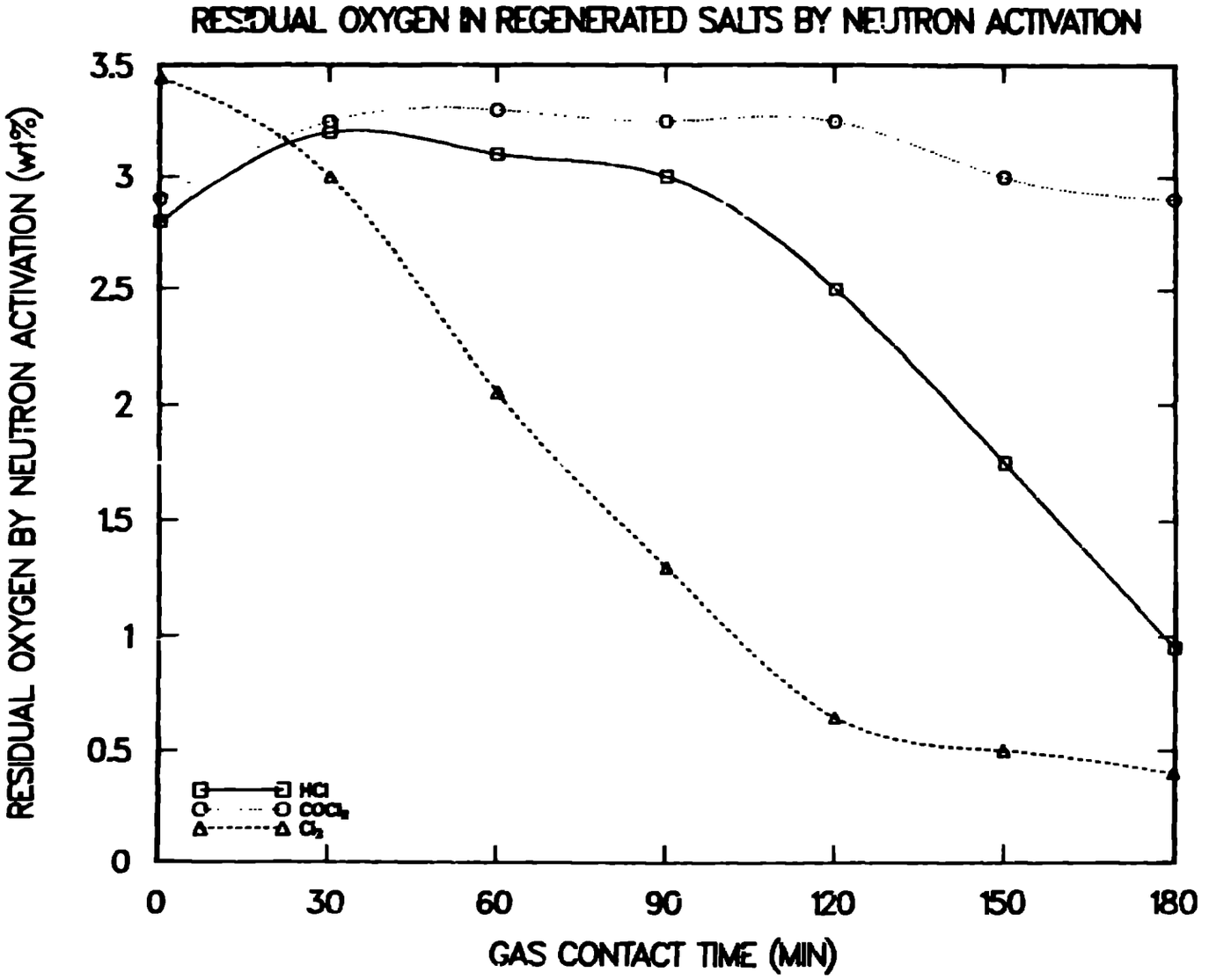


Figure 13: Residual Oxygen in Regenerated Salts by Neutron Activation

oxygen, no clear reduction is observed until after 90 minutes of contact time. Virtually no oxygen decrease is apparent from the phosgene samples. Work is continuing on the regeneration of spent oxide reduction salts using both HCl and chlorine.

These are two of the major new developments in the pyrochemical processing of plutonium at Los Alamos. These efforts have resulted in more rapid recycle of plutonium residues and will, hopefully in the near future completely eliminate one of our large volume residues.