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Plutonium Fluoride Reduction Slag

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Copyedited by Samantha Forrest

LA-9655-MS

UC-10
Issued: July 1983

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PYROCHEMICAL RECOVERY OF PLUTONIUM FLUORIDE REDUCTION SLAG

by

D. C. Christensen and J. A. Rayburn

ABSTRACT

A process was developed for the pyrochemical recovery of plutonium from residues resulting from the PuF_4 reduction process. The process involves crushing the CaF_2 slag and dissolving it at 800°C in a $CaCl_2$ solvent. The plutonium, which exists either as finely divided metal or as incompletely reduced fluoride salt, is reduced to metal and/or allowed to coalesce as a massive button in the bottom of the reaction crucible. The recovery of plutonium in a 1-day cycle averaged 96%; all of the resulting residues were discardable.

I. INTRODUCTION

Metallic plutonium was first prepared by R. D. Baker at Los Alamos, using the reduction of PuF_4 with calcium in a sealed pressure vessel.[1] The process is still one of the principal methods of producing metal. In the process, PuF_4, calcium, and iodine are heated in an MgO crucible that is sealed inside a heavy-wall, stainless steel vessel. A small amount of iodine and additional calcium metal are added to the reaction mixture as an initiator for the PuF_4 reduction. When heated to approximately 325°C, calcium and iodine react, liberating heat and adding energy to the PuF_4. The reaction is as follows:

$$Ca^{\circ} + I_2 \rightarrow CaI_2 \qquad \Delta H = -128 \text{ kcal/mole Pu} \quad . \qquad (1)$$

The heat immediately raises the temperature of the mixture, and the reduction of PuF_4 with calcium takes place at ∿600°C. The reaction is as follows:

$$PuF_4 + 2Ca^{\circ} \rightarrow 2CaF_2 \qquad \Delta H = -156 \text{ kcal/mole Pu} \quad . \qquad (2)$$

This reduction is also very exothermic and produces enough heat so that the temperature of the melt can increase to values as high as 2000°C. The resulting slag ($CaF_2 \cdot CaI_2$) melts at 1320°C. Because the melting point is well below the reaction temperature, the plutonium metal product collects as a metal button in the bottom of the crucible.

At Los Alamos, the PuF_4 feed material is made by the hydrofluorination of PuO_2 at 600°C. The reaction is as follows:

$$PuO_2 + 4HF \rightarrow PuF_4 + 2H_2O \quad . \qquad (3)$$

The extent of this reaction is not always complete and, consequently, the feed to the reduction step often contains a small amount of PuO_2. In the reduction, the PuO_2 is converted to metal by the following reaction:

$$PuO_2 + 2Ca^{\circ} \rightarrow Pu^{\circ} + 2CaO \qquad \Delta H = -51 \text{ kcal/mole Pu} \quad . \qquad (4)$$

The heat released from this reaction is much less than that from the PuF_4 reduction. The overall thermal yield during the reduction is decreased because more plutonium is fed as PuO_2 than as PuF_4.

If the thermal yield is insufficient to melt the slag by-product, then all or part of the plutonium metal is held up in the slag as plutonium metal powder or finely dispersed metal beads. This results in a reduction misfire.

Periodically, during the metal preparation sequence, there are reduction misfires in the fluoride-reduction step. Historically, these residues have gone to the slag-and-crucible dissolvers to be dissolved in acid and run through the aqueous processing sequence. This sequence is time-, space-, and labor-intensive and therefore is a costly route.

To circumvent the costly aqueous sequence and return this material to the metal process stream as rapidly as possible, we have developed a pyrochemical process to treat slag residues from the fluoride-reduction step. The process has been performed using the misfired slags but is not restricted to these high-plutonium-bearing residues.

II. PYROCHEMICAL RECOVERY

In the fluoride-reduction step, iodine is added to the reaction mixture as an initiator. Only a small quantity of iodine is needed; therefore, the resulting slag contains only about 5% CaI_2. In the evaluation of the pyrochemical recycle of these slags, CaI_2 in the slag is not significant. Therefore, in the following discussion, the existence of CaI_2 is ignored.

Because we want to convert 100% of the PuO_2 to PuF_4 and feed this material to fluoride reduction, we started our alternate recovery investigation assuming that the slag was 100% CaF_2. The way to insure complete recovery of the plutonium metal from the slag is to provide an all-liquid system, thus allowing the plutonium to coalesce in the bottom of the crucible. We therefore looked at a number of solvents for one that would reduce the melting point of the misfired slag.

We specifically wanted a fused halide salt that could dissolve the CaF_2 and remain liquid at low temperatures (<800°C). The prime candidate was $CaCl_2$. Figure 1 shows the $CaCl_2$-CaF_2 phase system, which has a low-melting eutectic (645°C) at 18.5% CaF_2 and a peritectic (735°C) for the 45% CaF_2 mixture. A 50:50 mole% mixture of the two salts melts at 800°C. Therefore, if we use $CaCl_2$ as a solvent/diluent in a quantity greater than 50 mole%, it will achieve our goal of providing a low-temperature liquid phase from which the liquid plutonium metal can settle.

III. EXPERIMENT DESCRIPTION

A. Experimental Plan

We anticipated several problems in achieving good recovery of plutonium:

- mixing of the multiple-phase system for achieving complete dissolutions of the CaF_2;
- coalescing of the plutonium metal in a dense, easily isolated mass; and
- generating a residue that requires no further processing and can be discarded.

The typical CaF_2 slag contains approximately 850 g of CaF_2, or approximately 11 moles. The minimum amount of $CaCl_2$ is, consequently, 11 moles or 1220 g.

To insure that all of the CaF_2 is dissolved at the desired 800°C operating temperature, more than 11 moles is added. This lowers the melting point of the binary salt mixture and forces the system into the liquid envelope region of the

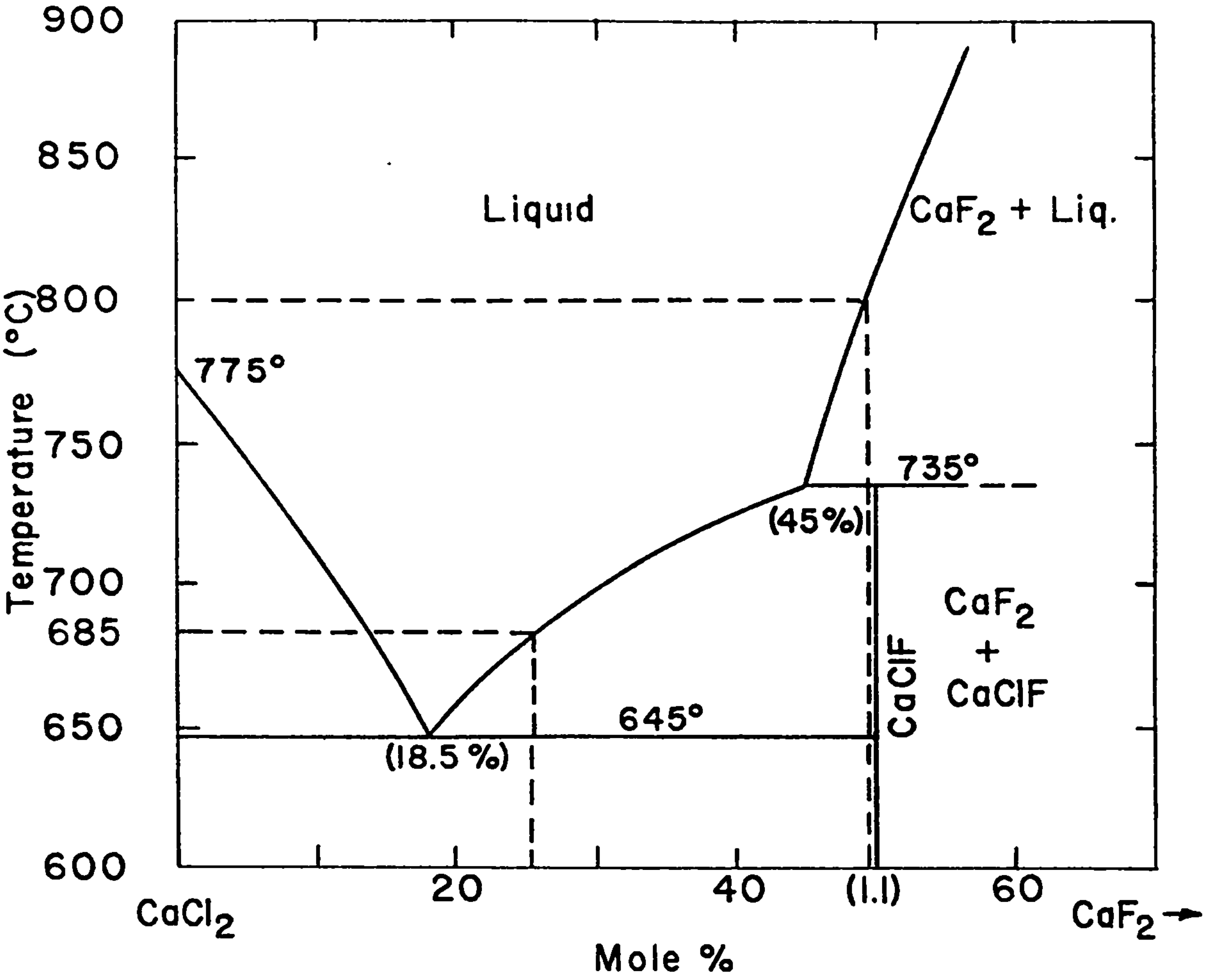

Fig. 1. $CaCl_2$-CaF_2 phase diagram.[2]

phase diagram. We optimized the process crucible by adding $CaCl_2$ to the operating level of the crucible. We found that approximately 3600 g of $CaCl_2$ could be used. The resulting mole ratio of $CaCl_2$ to CaF_2 was 3:1, or 75% $CaCl_2$ and 25% CaF_2. The melting point of this mixture is 685°C, which is well below the 800°C operating temperature.

The rate of dissolution, as well as the coalescence of the product metal, is highly dependent on mixing. Thorough mixing can be achieved by proper design and operation of the agitator or stirrer. Quantitative collection involves many parameters, such as crucible geometry, stirrer configurations, stirring rate, and temperature.

Most of the development work was performed in the metal production facility using one of the standard plutonia-reduction furnaces. The objectives were to

- develop the recovery process,
- demonstrate a rapid and less costly turnaround of plutonium metal in our residues, and
- be able to discard the resulting residues without further processing.

B. Equipment

The equipment used for the pyrochemical slag recovery (Fig. 2) is a clam shell furnace wrapped around a 6-in.-o.d. furnace tube. Inside the furnace tube is a Ta-10W stirrer, a tantalum and nickle thermocouple sheath, and an MgO reaction crucible. The reactants are placed inside the MgO crucible, which is placed inside the furnace tube. The furnace tube is then evacuated and filled with argon to 3 psig. The furnace is heated at a maximum rate of 200°C/h to the melting point of $CaCl_2$ (775°C). Both the thermocouple sheath and the stirrer are then lowered into the melt. The stirrer is activated when the melt temperature reaches 800°C. The stirrer is run at 600 rpm for 15 min, then raised approximately 1 in. off of the bottom and run at 100 rpm for 2 min. Upon completion of the stirring cycle, the stirrer and the thermocouple sheath are raised from the melt and the furnace is cooled to room temperature. The MgO crucible is then removed from the furnace and the metal button is removed from the salt.

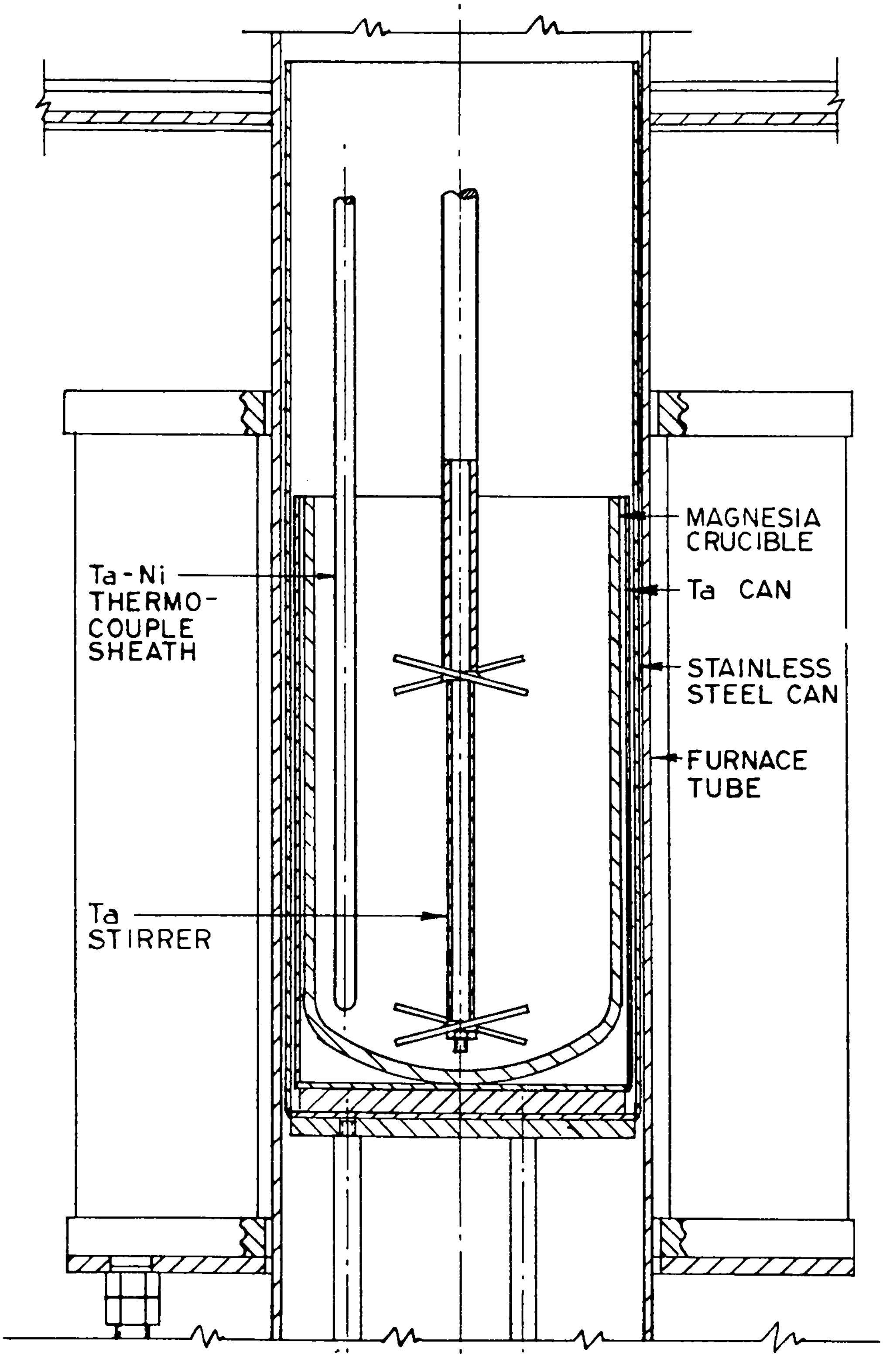

Fig. 2. Schematic of equipment used for the pyrochemical recovery of fluoride-reduction slag residues.

C. Reagents and Materials

- Calcium--Calcium metal is used in both the fluoride-bomb reduction step and in the slag recovery step. The calcium is Pfizer's redistilled grade 6-mesh nodules.
- $CaCl_2$--$CaCl_2$ is used as the solvent in the slag recovery step. The $CaCl_2$ is Malinckrodt 4880, food grade.
  It is dried under vacuum at 225°C for 7 days; then it is isostatically pressed into 3.6-kg cylinders.
- Crucible--The crucibles used in the study are fabricated by Honeywell Ceramics, Inc. They are MgO with up to 3 wt% Y_2O_3.
- Stirrers--The stirrers are fabricated at Los Alamos. They are made of 0.50-in.-diam Ta-10W rods with 0.125-in-thick Ta-10W blades welded in place.

IV. RESULTS OF PYROCHEMICAL SLAG RECOVERY

Six runs were performed to recover the plutonium from misfired fluoride-reduction runs. In all cases, the slag was first crushed with a hydraulic ram to as small a particle size as possible to provide a large surface area for $CaCl_2$ attack. The slag was loaded into a crucible with 160 g of calcium metal. The calcium was added to reduce any unreduced PuF_4 or PuO_2 in the slag and to assist in the coalescence of the plutonium metal. A $CaCl_2$ salt cylinder (average weight of 3493 g) was placed on top of the calcium metal. This whole assembly was then placed in the furnace tube and heated to the reaction temperature (800°C). Stirring was performed at 800°C according to the experimental plan. Table I shows the processing results for all six runs.

The following is a summary statement for each run.

- Run XBR-XP--A total of 336 g of plutonium was carried over in the slag from the fluoride reduction. Slag recovery yielded a button. A thermal neutron count (TNC) of the $CaF_2/CaCl_2$ crucible residue showed that all but 2 g of the plutonium was recovered in the metal. This represented a 99.4% yield. The button separated cleanly from the salt. The button and salt appeared very similar to the residue from a normal direct-oxide-reduction run. All residues were discardable.

TABLE I

PYROCHEMICAL SLAG RECOVERY TEST RESULTS

Run XBR	Slag Wt (g)	CaF (g)	CaCl (g)	Pu Feed(g)	Ca Feed(g)	Pu Prod(g)	Yield %	Ca Residual	Disposition of Residues
XP	1177.4	841.4	3600	336	160	334	99.4		Below discard limit* Sent to retrievable storage
180	1823	876	3575	947	160	798	84.3	190	Insufficiently crushed feed Residue went to secondary recovery
172	1573	784	3574	789	160	763	96.7	187	Below discard limit* Sent to retrievable storage
193	1642	1284	3279	58	160	355	99.2	109	Below discard limit* Sent to retrievable storage
192	1723	1212	3549	511	160	475	93.0	130	Below discard limit* Sent to retrievable storage
183	1281	1030	3381	251	160	238	94.8	106	Below discard limit* Sent to retrievable storage
6-run average	1537	1004.6	3493	532	160	492	92.5		
5-run average (excluding XBR-180)	1480	1030	3477	449	160	431	96		

*The discard limit for fused chloride-melt salts is set at 13.46 g of plutonium per kilogram of bulk weight. This has been established as the economical limit so that the cost of processing equals the value of the recovered residue.

- Run XBR-180--A total of 947 g of plutonium was fed to the slag recovery process. The slag was inadvertently loaded as golf-ball-sized chunks instead of being crushed to a powder. The mix was run up to 900°C and slowly swirled for 2 h to enhance dissolution of the CaF_2. After 2 h, chunks could still be detected in the crucible. After being cooled and unloaded, the metal button broke away very cleanly from the salt. The bottom half of the salt had a dark brownish hue that changed to a very light color at the top. The plutonium distribution was as follows: 798 g in the button (84.3% yield), 14 g in the upper half of the salt, 4 g in the crucible, and 131 g in the lower half of the salt. A calcium button, weighing 190 g, was found on top of the salt.

- Run XBR-172--A total of 789 g of plutonium was fed to the slag recovery process. All slag was crushed except some chunks that resisted complete crushing. The furnace was run up to 900°C and stirred slowly for 15 min. After being cooled and unloaded, the metal button broke away very cleanly from the salt. The salt was a single, homogeneous, light color. A TNC of the residue showed that 20 g of plutonium remained in the salt and 6 g remained in the crucible. The button contained 763 g of plutonium, or 96.7% yield. All residues were discardable. A calcium button, weighing 187 g, was found on top of the salt.

- Run XBR-193--A total of 358 g of plutonium was fed to the slag recovery process. The slag was crushed completely before loading. After being stirred at 800°C for 15 min, the salt was allowed to cool. When unloaded, the metal button broke away very cleanly from the salt. A TNC of the salt and crucible residues showed that only 3 g of plutonium remained uncollected. The plutonium in the button was 355 g, or 99.2% yield. All residues were discardable. A calcium button weighing 106 g, was found on top of the salt.

- Run XBR-192--A total of 511 g of plutonium was fed to the slag recovery process. The slag was crushed completely before loading. The charge was stirred at 825°C for 15 min. After being cooled and unloaded, the button broke away very cleanly from the salt. A TNC of the residues showed that 33 g of plutonium remained in the salt and 3 g remained in the crucible.

The button contained 475 g, or 93% yield. All residues were discardable. A calcium button, weighing 109 g, was found on top of the salt.

- Run XBR-183--A total of 251 g of plutonium was fed to the slag recovery process. The slag was crushed completely before loading. The charge was stirred at 800°C for 15 min. After being cooled and unloaded, the button broke away very cleanly from the salt. A TNC of the residues showed that 13 g of plutonium remained in the salt and no plutonium remained in the crucible. The button contained 238 g, or 94.8% yield. All residues were discardable. A calcium button, weighing 130 g, was found on the top of the salt.

V. DISCUSSION OF RESULTS

In one of the six cases (XBR-180), the slag was improperly crushed before being loaded into the crucible. After 2 h of slow stirring at 900°C, all of the CaF_2 had not dissolved into the $CaCl_2$. In this run, the product yield suffered because of the failure to release the plutonium from the high-melting CaF_2. This indicates that the dissolution of a massive piece of CaF_2 into $CaCl_2$ is very slow. Crushing the slag greatly enhanced the dissolution. With this single exception, all runs produced a discardable residue, with the average recovery yield being 96%. The CaF_2 was successfully dissolved in the $CaCl_2$, thus releasing the trapped plutonium.

In all runs, a sizeable calcium metal button was found at the top of the salt residue. The buttons ranged in size from 190 g to 106 g. Such a large calcium excess indicates that additional calcium metal may not be needed to facilitate the recovery of plutonium from the slag. In half of the runs the calcium residue was smaller than the 160-g reduction charge, indicating that some of the calcium is being used for reduction purposes.

The solubility of Ca° in $CaCl_2$ is approximately 1 wt%; this means that up to 36 g of Ca° should dissolve in the solvent salt. During the fluoride-reduction step, an excess of calcium is used. This excess is carried over into the slag recovery step, and with the 160 g of new Ca°, saturate the $CaCl_2$ solvent and provide a more than enough reducing agent in the slag recovery step. Since there is such a large excess of Ca° after slag recovery, future tests will be performed using less calcium.

VI. CONCLUSIONS

A simple procedure was developed to rapidly recover the plutonium from fluoride-reduction slag residues. Crushed CaF_2 slag was dissolved in $CaCl_2$ at 800°C, and the residual plutonium was recovered either by coalescence of finely divided metal beads or by the reduction of incompletely reduced plutonium salts. A large calcium residue was observed at the end of each run. The principal mechanism for the recovery is therefore assumed to be the coalescence of finely divided plutonium metal in the slag.

In one case, the CaF_2 was fed as golf-ball-sized fused chunks. After 2 h of slow stirring at 900°C, the CaF_2 remained incompletely dissolved. As a result, the residue after the run retained a significant amount of plutonium.

In the five cases where the CaF_2 was crushed, the average recovery yield of plutonium was 96%, with the high being 99.4% and the low being 92.5%. In all five cases the salt residues after recovery were well below the discard limits and were sent to retrievable storage.

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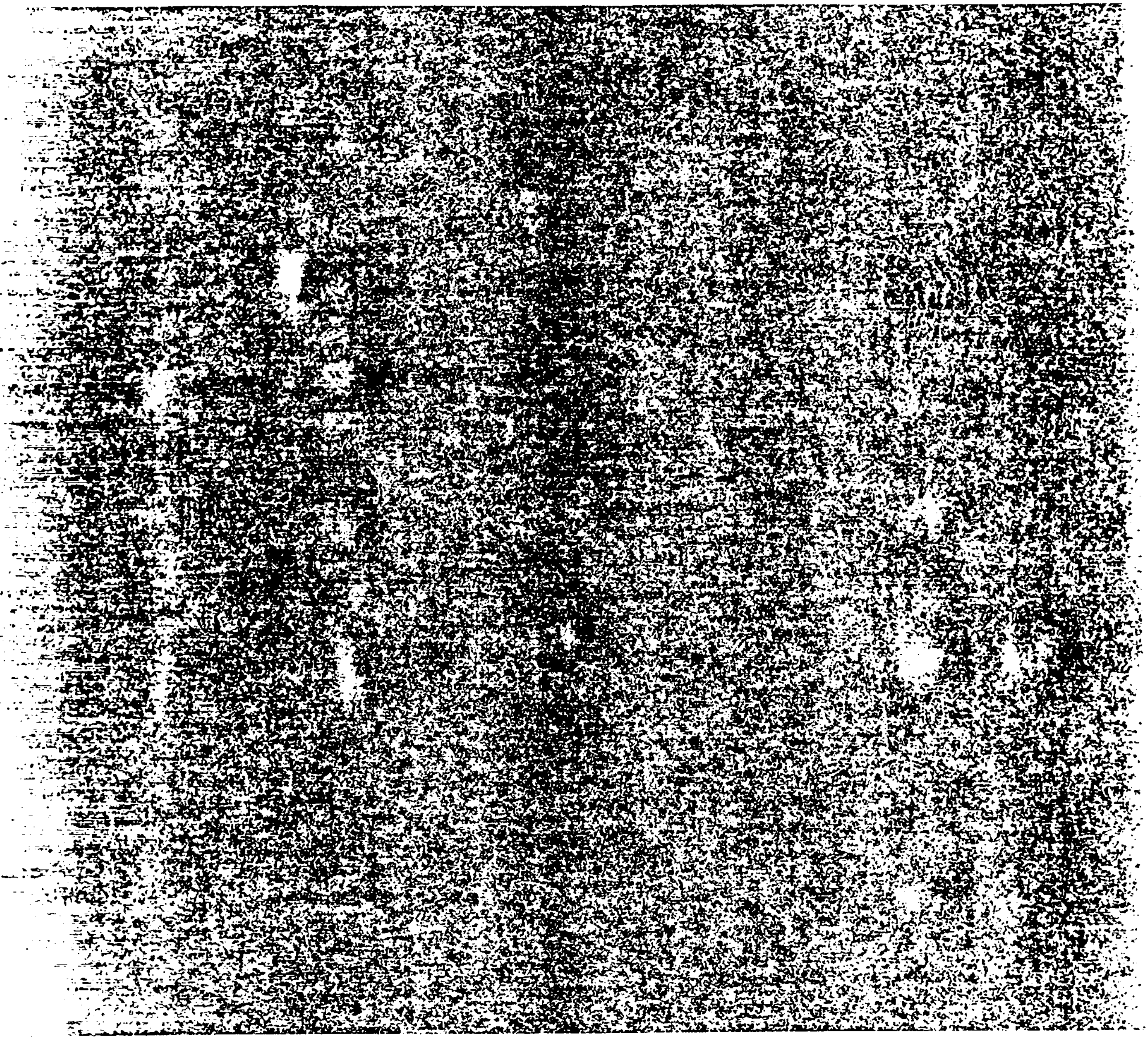

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