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TRIP REPORT - MALLINCKRODT CHEMICAL WORKS AND KNOLLS ATOMIC POWER LABORATORY DISCUSSIONS OF URANIUM REDUCTION PROBLEMS

INTRODUCTION

Metallurgy Research at Hanford has been investigating the reduction of various uranium coumpounds to metal. The concept of the U-Mg matrix fuel element has resulted in an even more vigorous effort toward preparation of spherical uranium shot. Efforts have been directed in two veins: one, the preparation of shot via reduction reactions; and two, via shot towers and other physical methods of converting massive uranium to particulate metal. In conjunction with development at HAPO on these problems, KAPL has also been conducting an investigation of the bomb reduction of uranium trioxide with calcium and the fabrication of the U-Mg fuel material by hot pressing techniques.

During the reduction of uranium tetrafluoride at the Mallinckrodt Works, about five percent of the uranium remains in the slag as pellets. Since tons of the shot embedded in the slag have been stored for lack of a use for the material, this slag offers an immediate supply of particulate uranium for fuel element development work. Dr. W. M. Leaders and group are cleaning some of this metal shot for shipment to HAPO.

The purpose of this trip was to discuss the mutual problems involved in the bomb reduction of uranium oxides, the slag leaching operation, and the classification procedures with Dr. A. P. Beard at KAPL. It appeared desirable also to visit the Mallinckrodt Works to become familiar with the large scale uranium reduction equipment and to discuss the separation problems involved in recovering shot from the fluoride slags.

VISIT TO MALLINCKRODT URANIUM WORKS

A. Trip Through Reduction Facilities - W. Petty

A brief description of the metal reduction facilities may be of interest. At the present time 300 pound charges of uranium tetrafluoride are being routinely fired. The tetrafluoride is prepared by ammonia reduction of uranium trioxide and subsequent hydrofluorination of the dioxide. Magnesium is used to reduce the uranium tetrafluoride to metal which is coalesced in a button called "the derby". The bomb itself is made of 3/4" boiler plate and is useable 40 to 50 times. Cost of each reduction bomb is about $150. Magnesium fluoride formed from the reduction of uranium tetrafluoride is used as a bomb liner. The fluoride is balled and cleaned of large uranium metal pieces which had not coalesced. A liner is then jolt-packed around a tapered mandrel centered in the bomb. Uranium tetrafluoride with a stoichiometric plus four percent excess of magnesium is packed in the lined bomb. This charge is fired by soaking the bomb in a 1300 F, 705 C, resistance furnace about three and one-half hours. The bomb is not hermetically sealed. A steel lid bolted to the bomb does, however, restrict gas flow and transient pressures of 50-80 psi have been estimated compared to 100-150 psi in a sealed reactor. After reaction, the bomb is cooled to 700 or 800 F or 370 to 427 C, by forced air and quenched in water. A two-hour pickle in 45 percent nitric acid is employed to clean up the derby before casting. Four pickled derbys are cast in vacuo from and into a magnesium oxide coated graphite crucible. Metal temperatures of about 2600 F are attained before the pour. The uranium ingot is a cylinder approximately nine inches in diameter and 48" long. This ingot is cleaned and sent to the rolling operation for slug fabrication. An all-out development effort on the Weldon Springs Plant is underway at Mallinckrodt. While the present reduction charges yield a 300-pound uranium derby which is cast into 1200-pound ingots, the Weldon Springs reduction will scale up to a 3300 pound "dingot". The word "dingot" has been used to designate an ingot cast directly from the reduction reactor or a direct ingot. Prior to work on the 3300-pound dingot, the 1400-pound dingot reaction was under study. The firing times for the 1400 and 3300 pound dingots are 5 1/2 - 6 1/2 hours and 8-10 hours, respectively. This compares to 3 1/2 hours in the 300 pound charges. Efficiency of the 1400-pound reduction was 96 to 97 percent. As of June 7, 1955, nine 3300 pound reductions had been fired. Yields ranged from 93-97 percent. Results are encouraging and all available time is being spent on the development of the large dingot process.

It was pointed out by Mr. Petty that the pickling step in the present process using 45 percent nitric acid results in a six percent uranium loss. However, an increase of six and one-half percent is realized in ingot yield from the casting operation.

The question of what factors generally seem to result in poor yields in the reduction of uranium tetrafluoride was asked. Mr. Petty stated that charges containing small amounts of UO_2F_2 + UO_2 gave varying results:

Charge Composition	Reduction Efficiency
1) UO_2F_2 High or about 3% UO_2 High or about 3%	Clean metal, high yield
2) UO_2F_2 High 3% UO_2 Low - much less than 3%	Clean metal, high yield
3) UO_2F_2 Low - much less than 3% UO_2 High 3%.	Poor metal, lower yields

In all three cases the firing time was long compared to the normal three and a half hours required with the 300 pound charges.

Calculations and experimental determination of the maximum temperatures attained in the production bombs indicate temperatures of 3000-3100 F and 3400 F, respectively. The higher temperatures obtained experimentally were made by adding capsules of oxides of different melting points to the charge and pin-pointing the maximum temperatures in this manner. The feeling is that the calculated temperatures are at present more accurate than the experimental.

Some development work has been done on recovery of uranium metal obtained from ingot scalping. Burning the metal to U_3O_8 for rehydrofluorination and briquetting the pieces for recasting have been considered.

B. Discussion with J. W. Stevenson and F. W. Frey

I was able to talk briefly with people in research and development about bomb reduction problems. Prior to the effort on the Weldon Springs Plant, small scale reduction reactions were being investigated.

Fred Frey felt that the more rapid heating of the small charges tended toward massive metal and had noticed that dolamite additions decreased the yield of massive metal.

Reductions of uranium oxides on a small scale gave metal shot instead of a button. F. W Frey has reduced UO_2 with magnesium in a CaF_2-MgF_2 eutectic slag. The small approximately 1/16 inch uranium spheres were not separated from the slag. Yield was low as much unreacted oxide was found. Similar results were obtained reducing UF_4 with magnesium in the CaF_2-MgF_2 eutectic slag. Frey had started a program to determine the MgO-MgF_2 phase diagram The only data obtained is that 15 w % MgO in MgF_2 produces a slag with a melting point above 1300 C.

J. W. Stevenson has heated UF_4 plus magnesium charges to temperatures just below the firing point and has then quick chilled the bombs. Often the reaction continues, however, in cases where firing was prevented, UF_3 is formed 2-3 minutes before firing. Thus, the Δ H of reaction is spread out and heat produced in the bomb is less effective than if it were produced at one time. Various additives, as UO_2 and NaF, have been used to retard firing times. The thought is that these compounds film the magnesium

preventing the partial reduction to UF_3. Also, firing temperatures are raised from 450 C to as high as 700 C. Therefore, heat from reaction is not consumed in raising the charge to 700 C. Likewise, additions of water, 100 grams/300 pounds of uranium delay firing time and results in higher yield.

Stevenson remarked that compressing the UF_4 charges appeared to have little effect on the yield except that less metal could be produced in any given bomb if it were loosely packed.

Purging the UF_4 charges with inert gas prior to firing seems to give slightly better metal. However the improvements in quality and yield do not warrant purging the 300-pound charges which are presently fired.

C. Discussion with W. M. Leaders

Hanford Metallurgy Research has received 20 pounds of shot from Mallinckrodt. The pellets were badly crushed during rolling clean-up operations. Dr. Leaders is planning to send several hundred pounds of pellets to Hanford in the future. Several inches of the slag just above the dingot and derby apparently contain most of the uncoalesced pellets. This material will be jaw crushed and then added to a ball mill. Using the uranium pellets as the balling material, the magnesium fluoride slag should powder and then can be separated by sieving. By the first of July we should know if the pellets can be effectively cleaned in this manner. The question was raised about the possibility of fire during this operation. Apparently, the best extinguisher for uranium fires at Mallinckrodt has been magnesium fluoride so there is little concern in ball milling, the uranium containing, magnesium fluoride slags.

Dr. Leaders was pessimistic about controlling a reduction of UF_4 to yield pellets. He felt the yield of useable pellets would be low due to fines and massive metal formed. However, one method of eliminating the amount of massive metal formed in the UF_4 charges is to trigger the reaction without heating the charge. The physical methods of converting massive metal to shot appear much more promising than reduction processes according to Dr. Leaders. Mallinckrodt in conjunction with Metallurgy Research at Hanford is building a spinning plate shot tower. Dr. Leaders indicated trial runs would be made using inert atmospheres. Molten metal falling on the spinning plate should produce the desired shot.

It may be possible to reduce UO_3 with calcium on a three hundred pound scale at Mallinckrodt Works. An experiment of this nature may be of interest to us in the future. Dr. Leaders was concerned about trying a magnesium reduction of UO_3 because of possible high magnesium vapor pressures formed. He felt the only reason that excessive magnesium pressures were not found in the present reductions of UF_4 was the large volume reduction at firing which allows magnesium to condense on the colder portions of the bomb above the molten slag.

VISIT TO KNOLLS ATOMIC POWER LABORATORY

A. Bomb Reduction of UO_3 with Calcium, A. P. Beard

Dr. A. P. Beard and F. K. Huemann have been reducing uranium trioxide with calcium. Efforts have been to increase the yield of pellets of -20 +100 mesh. Four kg of

uranium oxide is the largest charge that has been reduced to date. The oxide reduction program at Hanford has been studied primarily on a 20-gram scale with a few reductions run on the 400-gram scale.

The four kg reduction bomb in use at KAPL is made of seamless heavy duty steel pipe of about 5 3/4 inches I.D. A steel plug and flange have been welded on to complete the assembly. An 18-inch magnesia crucible is being used as the liner. The bomb is hermetically sealed using a heavy 3/4 inch, copper gasket with a bolt-down steel lid. The gasket edges are machined after each firing and the gasket re-annealed. No life expectancy has been assigned to the bombs; however, they have been used 30 to 40 times. The charges are fired with a 10,000 cycle, 15 KW induction furnace in a brick room with a blow-out wall. Personnel can observe recorded bomb wall temperatures and induction generator power behind the brick partition. The coil being used is made of 1/2 inch copper tubing. Only the lower half of the bomb is being heated. The bombs are vacuum purged with argon or helium and leak tested prior to firing. An average heating rate of 100 C/minute has been used in essentially all charges fired. The initial rate is greater than this. At about the curie point the charges fire and coupling is much less effective. To date, the charges have been heated until firing occurred and heating continued until the temperature of the bomb wall started to decrease. The charges generally fire at bomb wall temperatures of 720-750 C. Maximum temperature attained is about 900 C. When a heating rate of 30 C/minute was employed, the charges fired at temperatures of about 640 C. Yields of +325 mesh uranium were smaller. Several intermediate rates between 30 and 100 C/minute were tested before the 100 C/minute rate was accepted as the most satisfactory. Percent excess calcium in the charge has been varied through 15, 30, 50, 60, and 70 percent. Some slight variation in yields of +325 mesh uranium were observed. Likewise, the mole ratio of $CaCl_2/UO_3$ has been varied. Best results were obtained using 50 percent excess calcium and a $CaCl_2/UO_3$ mole ratio of 0.84. The degree of subdivision of the $CaCl_2$ seemed to have no effect on the yield. Pressures within the bombs have not been measured. However, no difficulties were noticed in firing any of the charges even with UO_3 that was partially hydrated. The yield of +325 mesh uranium has varied considerably. Apparently drying the UO_3 at 450 C resulted in more reproducible results. Recovery yields are averaging about 90 percent. An average sieve analysis of the uranium particles from the dry UO_3 reductions follows:

Mesh Size	Yield
-325	45%
-100 +325	21%
-20 +100	21%
+20	13%

The +20 mesh material is often large with pieces weighing as much as 50 grams. Much of the smallest +20 material is not spherical. Dr. Beard feels there would be a market for any -325 mesh and for any +20 mesh uranium produced in the oxide reduction process.

Several charges of UO_3 mixed with UF_4 were fired. Large pieces of uranium were obtained in these runs which corresponded to the amount of uranium added as fluoride. The amount of -325 mesh material remained about the same. Reductions were made employing Ca-I_2 booster. Again, results were not greatly improved and reproducibility was much poorer. However, the boostered charges were fired with the moist UO_3.

An NaCl-$CaCl_2$ flux was employed in several UO_3 reductions. Yields were very poor and the NaCl additions were discontinued. A number of charges in which the $CaCl_2$, UO_3, and reductant were placed in the crucible in layers were fired. The homogeneous charges were far superior and layering of the reactants was discontinued. Charges were fired in which the reactants were compressed. This increased loading by a factor of one half but results were not quite as good as in the normal charges. Again, the undried UO_3 was used in these tests so a true evaluation of the briquetting of charges may not have been obtained.

The fused charge is removed from the bomb and leached in acetic acid. The pH of the leach solution is made 4-5 and the solution is cooled with ice. At present, the slag is not jaw crushed. The solid piece is placed in the leach tank for two to three hours. The uranium metal particles are wet sieved by hand and dried on a paper filter with ether or alcohol. A few uranium fires have occurred. However, the calcium deposited on the crucible lid has generally been more pyrophoric than the uranium fines. The leaching operation is straighforward but rather messy.

Little was known of the $CaCl_2$-CaO system except that 13.8 percent CaO was soluble in $CaCl_2$ at 900 C(1). No attempts have been made to learn more about the phase diagram of this system.

Dr. Beard hopes to be able to try Kg size reductions of UO_2-Cl_2. He feels that bomb reductions of this compound may produce massive uranium.

Modifications of the induction equipment at KAPL will now permit better coupling to the reduction bomb after the curie point has been reached. Some experiments will be run in which the charges are soaked at high temperature after firing. Dr. Beard appears extremely encouraged about the oxide reduction process. However, at the present the process is far from acceptable for large scale production of pellets. Apparently Dr. Beard reasons that any of the fines could be readily marketed for powder metallurgy uses while the massive pieces could be processed by casting facilities at various sites.

B. <u>Hot Pressing U-Mg Fuel Elements, R. N. Honeyman</u>

Mr. Honeyman has been involved in a program of preparing the U-Mg fuel pieces for the pile evaluation by Hanford personnel. A group of one-half inch diameter, 1-3/4 inch long pieces canned in zircaloy are being fabricated using particles prepared by Dr. Beard and Mr. Huemann. Three fuel capsules of coarse particles, three of medium, and three of fine particles were to be prepared. The uranium particle sizes are -20 +100, -100, +325 and -325 mesh, respectively. These fuel pins would contain about 65 volume percent uranium. Six high density capsules are being prepared. If the correct amounts of spherical particles with a ratio of diameters of 0.003 are packed together the density of the piece can be increased above the normal pack density of uniform spheres. Three fuel pieces of about 74 volume percent u ranium have been prepared

(1) Arndt, Kurt and Lowenstein, W., Zeitschrift Fur Elektrochemie, 15, p. 784 (1009).

using 60 percent -20 +40 mesh and 40 percent -325 mesh uranium pellets. The other three high density fuel pins will be prepared using the same uranium composition but with an excess of magnesium resulting in about 65 volume percent uranium in the fuel material. The high density pieces contain one to three percent void space. Mr. Honeyman was concerned about the effect of void space on in-pile performance of the fuel material. He was informed that one to two percent voids may be beneficial due to fission product build-up in the piece. The U-Mg fuel material prepared from -325 mesh uranium has not been satisfactory. Excessive voids have been found in several pieces while the few apparently sound elements began to deteriorate after a few days. Work is being continued on the preparation of these pieces. Mr. Honeyman has been removing magnesia, filter paper, and other solid material from the uranium fines by flotation. The uranium oxide skin can be effectively removed from even the -325 mesh uranium in dilute nitric acid. Bright uranium fines can be held in vacuum overnight with fair success. The clean uranium spheres and magnesium are cold pressed at four tons and this piece which can be handled is hot pressed at about 650 C and 4000 psi for thirty minutes. If the die is poor, there is some extrusion of magnesium. Aquadag lubricant seems to act as a seal and tends to prevent this effect.

Mr. Honeyman will attempt to hot press uranium zirconium at temperatures of 600 C. Zirconium has been compressed to essentially hundred percent densities at this temperature. Since uranium is above the alpha, beta transformation, it should resist flow and remain as discrete particles.

C. Electrolytic Reduction of Uranium, Dr. L. W. Niedrach

Dr. Niedrach and Mr. Dearing have been working on electrolytic reduction of uranium oxides and fluorides to metal. Container problems for fluoride and chloride slags have been a major problem. Graphite crucibles lined with UC_2 and UC have been prepared, but the carbide layer seems to break away from the graphite. Crucibles of cerium sulfide, boron nitride, silicon carbide, and silicon nitride are being investigated. Most of the work is being done in graphite for lack of a better material. A ten percent nickel-thorium alloy has been prepared by electrolytic reduction of thorium oxide. The low melting alloy is collected as a liquid at 950 C from a $LiF-ThF_4$ bath using a nickel cathode and graphite anode. Since the solubility of thorium oxide in the $LiF-ThF_4$ slag is low, the oxide is added to a perforated graphite compartment. This prevents an oxide sludge from forming on the bottom of the cell. Similar runs using uranium oxides have failed to yield metallic uranium or uranium alloys. Experiments are also underway on the electrorefining of uranium aimed at fission product removal. Uranium rod anode is added to a UCl_3-CaCl_2 bath at 950 C and a 15% nickel uranium alloy is recovered on the nickel cathode.

Several pellets of uranium have been prepared by electrolysis of UO_2 dissolved in fluoride slags at temperatures above the melting point of uranium. A helium atmosphere was employed in these experiments. Only a fraction of a percent yield was obtained up to extreme current densities. One large pellet of about 1/4 inch diameter has been recov...

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