

1966

## Cesium from Pollucite by Aluminum Reduction

W. A. Gault  
*Iowa State University*

T. L. Young  
*Phelps Dodge Research Laboratory*

H. A. Wilhelm  
*Iowa State University*

*Let us know how access to this document benefits you*

Copyright ©1966 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

---

### Recommended Citation

Gault, W. A.; Young, T. L.; and Wilhelm, H. A. (1966) "Cesium from Pollucite by Aluminum Reduction," *Proceedings of the Iowa Academy of Science*, 73(1), 81-96.

Available at: <https://scholarworks.uni.edu/pias/vol73/iss1/15>

This Research is brought to you for free and open access by the IAS Journals & Newsletters at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact [scholarworks@uni.edu](mailto:scholarworks@uni.edu).

**Offensive Materials Statement:** Materials located in UNI ScholarWorks come from a broad range of sources and time periods. Some of these materials may contain offensive stereotypes, ideas, visuals, or language.

# Cesium from Pollucite by Aluminum Reduction<sup>1</sup>

W. A. GAULT, T. L. YOUNG<sup>2</sup> AND H. A. WILHELM

*Abstract.* Aluminum metal was found to liberate cesium almost quantitatively from pollucite ore when reacted under conditions of operation determined by experiments described in the paper. In the treatment, ore ground to pass a 150 mesh sieve is mixed with atomized aluminum and the mixture heated under an inert atmosphere in a retort. Pollucite ore from one source yielded its cesium when treated at 950°C for 4 h while pollucite ore from another source required a temperature up to 1050°C to yield essentially all of its cesium. The cesium metal obtained from pollucite by aluminum reduction is about 90% pure; it contains small amounts of sodium, potassium, rubidium, lithium and other elements. Recovery of pure cesium from this product could be by fractional distillation or by further well established chemical treatments.

Metallic cesium was of interest only for laboratory studies until about 40 years ago when it was first used as a getter in radio tubes. Until relatively recent developments, however, its uses in photoelectric cells, infra-red viewing systems and a few other devices have constituted most of the requirements for the metal. The future possibilities of cesium metal in the development of power for certain applications point to a marked increase in the demand for that metal. However, present production is still on a relatively small scale and processes covering a wide range of chemical treatments are being employed to obtain cesium from its ore. The more important processes include acid leaching and direct metal replacement. The study reported here deals with cesium recovery from pollucite ore concentrates by treatment with aluminum metal.

Although small amounts of cesium occur in many minerals, pollucite is the only known mineral of high cesium content. A flotation method has been developed for concentrating pollucite from associated minerals<sup>1</sup> and the resultant ore concentrates usually contain 20 wt % or more cesium. Pollucite is considered by some to be represented by the chemical formula  $2\text{Cs}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{H}_2\text{O}$  while others represent pure pollucite as  $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ . The natural mineral, however, will contain considerable amounts of sodium, potassium and lesser amounts of rubidium replacing some of the cesium. The formula for the naturally occurring mineral containing sodium has been represented by  $(\text{Cs}_2\text{O})_{1-x} \cdot (\text{Na}_2\text{O})_x \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2x\text{H}_2\text{O}^2$  where x apparently ranges between 0.1 to 0.3. Although aluminum has been used to reduce free cesium oxide,<sup>3</sup> a literature

<sup>1</sup> Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1885.

<sup>2</sup> Phelps Dodge Research Laboratory, Morenci, Arizona.

search did not reveal the use of aluminum in liberation of cesium from compounds such as pollucite.

The acid leaching process is most commonly used for obtaining cesium from pollucite; a mineral acid, usually HCl or H<sub>2</sub>SO<sub>4</sub>, is employed. Cesium is subsequently precipitated from the leach solution as a double salt, generally as cesium antimony chloride 3CsCl · 2SbCl<sub>3</sub> or as cesium alum Cs<sub>2</sub>SO<sub>4</sub> · Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 24H<sub>2</sub>O. Treatment of either double salt can give a purified single cesium salt. For metal preparation, the cesium salt is ordinarily prepared as or converted to cesium chloride. Active metals are then employed to release cesium from its purified compounds. In a typical cesium metal preparation, purified cesium chloride obtained from the decomposition of the antimony double salt is reduced with calcium by heating in vacuum to yield the metal.

Experimental work on direct metal replacement employing a calcium reduction of pollucite in vacuum was reported by Hackspill and Thomas<sup>4</sup> in 1950. According to their report, one part by weight of pulverized pollucite ore, dehydrated at 900°C, is mixed with three parts of metallic calcium chips. As this mixture is heated in a vacuum, a reaction apparently starts near 750°C. With operating temperatures of 900°C, cesium yields of 85% are reported. Although this method appears interesting, the large excess of calcium used to release the cesium poses an economic factor for other than laboratory operations.

A sodium metal process for the direct extraction of cesium from pollucite has been briefly described.<sup>5</sup> According to this description, the ground ore was mixed with sodium and heated to liberate the cesium. The mixture was then cooled and a liquid alkali metal alloy containing cesium was filtered from the ore residue. It was claimed that this treatment removed about 90% of the cesium from the pollucite.

A recent patent for the direct extraction of cesium from pollucite covers the use of lithium, sodium or potassium.<sup>6</sup> One experiment using two parts metallic sodium by weight to three parts of pollucite has been described. About 88% of the cesium was extracted when this ore-sodium charge was heated for 31 h over temperatures ranging between 400 and 700°C under inert gas pressures of 75 to 250 mm.

Any process for cesium metal by direct reduction generally yields metal contaminated with the other alkalis and usually requires subsequent purification. Distillation has been employed in purifying the metal. The boiling points of the alkali metals are in reverse order of their atomic weights; therefore, rubidium (b.p. 694°C) presents the greatest problem in distilling cesium (b.p. 670°C) from the other alkali metals. However, a method of fractional distillation employing a stainless steel column<sup>6</sup> has

produced pound quantities of metallic cesium containing less than .02 wt % other alkalis.

A preliminary investigation of various means for treating ore to recover cesium led to the present study which has been focused essentially on the release of cesium from pollucite ore by a reactive metal. The release of the cesium as metal from the ore combined with the fractional distillation could give an over-all process for pure metallic cesium. If the cesium is released from the ore in a condition that cannot effectively lend itself to fractional distillation, then the recovery of purified cesium metal would involve chemical processing of the released product. These chemical treatments would involve solution followed by such operations as precipitation, liquid-liquid extraction or ion exchange to give a purified cesium compound. The purified cesium metal would then be obtained by treatment of this compound with an appropriate reactive metal. Regardless of whether the cesium released from the ore is to be purified either by distillation of the metal or by chemical processing, the evaluation of the over-all process depends primarily on the effectiveness with which the cesium is released from the ore.

The major part of this investigation on cesium removal from pollucite was performed with an ore from Southern Rhodesia which was obtained from the American Potash and Chemical Corporation. A domestic pollucite from Tin Mountain Mine near Custer, South Dakota was employed in only a few tests. Unless otherwise specified, the ore from Southern Rhodesia was employed in the experiments. Ores from both sources have been analyzed by a number of laboratories and the average values of the constituents are recorded in Table I. These ores were received in the form of small lumps; for the experiments, they were ground in finer sizes in a laboratory mill.

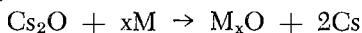
Table I. Analyses of Pollucite Ores

Constituent	Southern Rhodesia Ore	South Dakota Ore
Cs <sub>2</sub> O	24.1 wt %	28.5 wt %
Rb <sub>2</sub> O	0.9	0.1
K <sub>2</sub> O	1.5	0.7
Na <sub>2</sub> O	2.3	2.7
Li <sub>2</sub> O	0.5	0.2
MgO	0.0	0.3
CaO	0.1	0.7
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.2
Al <sub>2</sub> O <sub>3</sub>	18.3	17.6
SiO <sub>2</sub>	47.7	45.8
L.O.I.	2.1	3.2

#### EXPLORATORY

Exploratory experiments on the removal of Cs from pollucite ore included treatments with anhydrous and aqueous hydrogen

fluoride, treatments with sulfur chloride, and direct reductions with carbon and metal reducing agents. The hydrogen fluoride treatments decomposed the ore but the fluoride products could not be readily processed. The sulfur chloride treatment was successful in bringing cesium to a recoverable form.<sup>7</sup> The carbon reduction in vacuum or inert atmosphere appeared to require rather high temperatures to release appreciable amounts of cesium. Some metallic reducing agents, however, were found to liberate cesium from the ore at temperatures below 1000°C. The metals used in these tests were selected on the basis of thermodynamic, economic and other practical considerations. Since free-energy data were not available on the cesium containing mineral, data<sup>8</sup> on pure cesium oxide were employed in the calculations to give indications of the thermodynamic potentials of the reducing metals relative to one another. The equations employed in these calculations are represented by



where "M" is the reducing metal considered for reaction with the pollucite. The results of the calculations of the free-energy change for the reaction of each of the reducing metals per mole of Cs<sub>2</sub>O at various temperatures are shown by the graphs in Fig. 1.

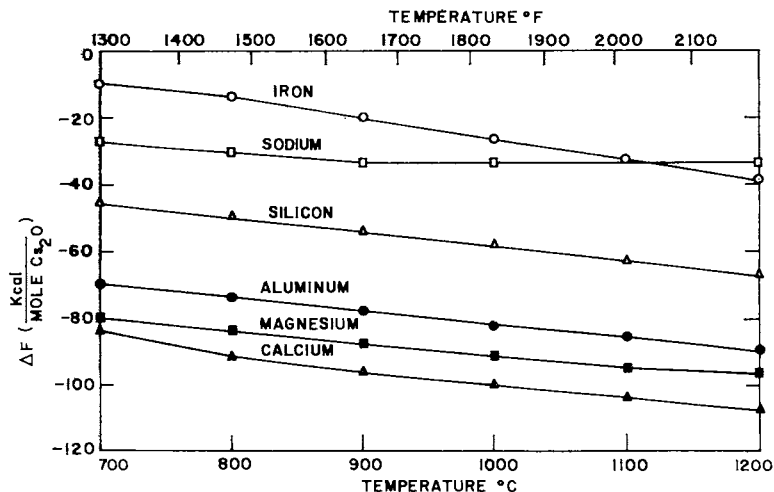


Figure 1. Free-energy vs temperature relationships for reactions between cesium oxide and reductants.

Of the six metals considered in this figure, iron appears to be the least favorable on the basis of free-energy change for the reduction reaction. The use of calcium and sodium in the removal of cesium from pollucite has been studied by others and

their findings have been briefly referred to above. The exploratory tests on direct metal reduction were then limited to the use of silicon, magnesium and aluminum. The results of the exploratory work with these metals led to the selection of the particular reductant to be employed in the present investigation.

On the basis of the free-energy relationships shown in Fig. 1, it appears that silicon is a potential reductant for cesium oxide; however, a test on a charge of pulverized pollucite ore with excess free silicon metal failed to release cesium when the charge was heated to 950°C under an inert atmosphere. Magnesium and aluminum were both found to react with the ore and produce good yields of cesium when the charges were treated in the same manner as with silicon. An exothermic reaction between the Southern Rhodesia ore and metal in the charge was observed for magnesium at about 575°C and for aluminum at around 825°C. Aluminum was found to react with other oxides in the ore, especially with the  $\text{SiO}_2$  component. Magnesium appears to be very effective in releasing cesium; however, it also reduced other constituents of the ore and gave side reactions to form magnesium silicides. Further investigation of the use of magnesium was tentatively set aside and aluminum was selected as the metal reductant to be employed in the work reported here on the treatment of pollucite ore.

For the reaction between aluminum metal and the ore, the reduction of other oxides including the reduction of all alkali metal oxides must be considered. Since Fig. 1 is based on free energies of formation of the oxides involved, the relative positions of the graphs for any two metals in the figure indicate also the relative free-energy values for reactions involving these two metals and their oxides. The graph for aluminum in Fig. 1 lies well below those for silicon and iron; it appears, then, that aluminum would tend to reduce the silicon and iron oxides as well as the cesium and other alkali metals in the ore.

The aluminum to ore ratio for a reduction charge is related to the purity of the aluminum and the composition of the pollucite ore. On the basis of the composition indicated in Table I for the Southern Rhodesia ore and assuming stoichiometric and complete reduction, 100 g of this ore would require approximately 34 g of pure aluminum metal. To release the cesium and other alkali metals would require only 3 g of this total. However, that required to reduce the  $\text{SiO}_2$  would be 29 g, and roughly 2 g would be required to react with the L.O.I. ( $\text{H}_2\text{O} + \text{CO}_2$ ). This amount is only indicative of the range of the aluminum to ore ratio that might be expected for this particular ore. A variation in ore composition, incompleteness of the assumed reactions and

other factors leave the optimum aluminum to ore ratio to be determined experimentally.

Exploratory tests were made on the reduction of the pollucite ore by aluminum in different forms. Aluminum as chunks, turnings or flake bronzing powder did not liberate cesium adequately from the ore. Good yields of cesium were obtained, however, when a granular type aluminum powder was employed as the reductant. The particular grade of this powder that gave efficient reduction is known as Alcoa Atomized Aluminum Grade 120. This particular grade of aluminum was adopted for use in subsequent tests in this study on the removal of cesium from pollucite ore. A sieve analysis showed that all of this aluminum passed a 40 mesh, 80% passed a 100 mesh and 40% passed a 325 mesh sieve. Chemical analysis indicated that the oxide content was such that the active aluminum metal was approximately 97%. On this basis, 35 g of this aluminum would be the minimum amount required to reduce the constituents in 100 g of the particular ore as considered above.

Further tests using the Alcoa aluminum, an argon atmosphere, Southern Rhodesia ore ground to pass 150 mesh and 4 h at temperatures below the limit of an ordinary electrical resistance furnace (1050°C) indicated that the aluminum reduction could offer a feasible means for recovery of cesium from pollucite ore.

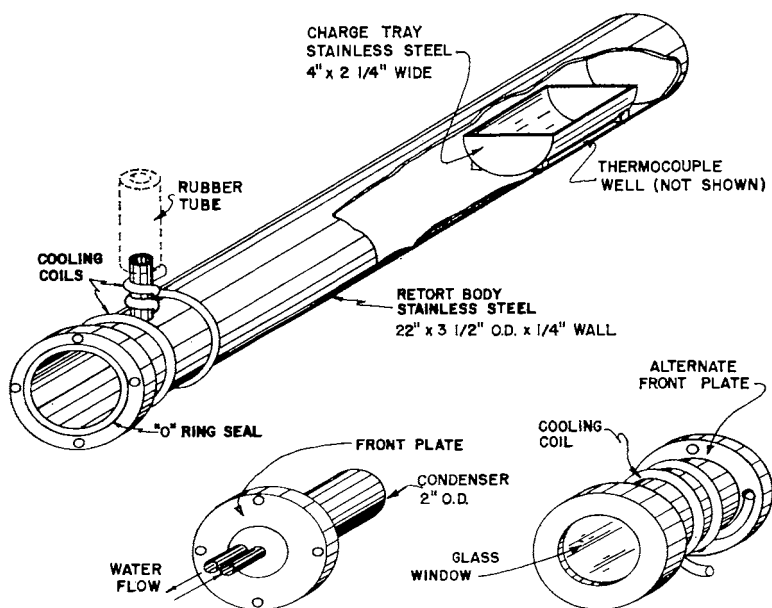


Figure 2. Perspective drawing representing reaction retort and accessories.  
<https://scholarworks.uni.edu/pias/vol73/iss1/15>

## APPARATUS

The retort and accessories used for studying the reaction between aluminum and pollucite are illustrated in the next three figures. Figure 2 shows the design of the retort body which was fabricated from stainless steel Type 309 Cb and the design of charge trays and front plates that were made from stainless steel Type 316. A rubber O-ring was employed as the seal between the retort and either front plate. As illustrated in the figures,  $\frac{1}{4}$  in. copper tubing was wrapped around one end of the retort as a means for water cooling this area in order to assist in condensing the metal vapors and prevent overheating the rubber seals and connections. One front plate was equipped with a water-cooled condenser while the alternate front plate provided a glass window for visual observations inside the retort during the progress of a treatment. Two thermocouples were inserted into a 7 in. long thermocouple well welded to the outside of the retort in the region of the charge. One of these thermocouples was connected to a West Model JP controller that governed the heating of the furnace. The other thermocouple was connected to a Bristol strip chart temperature-time recorder.

As illustrated by the photograph of Fig. 3, the retort (A) was positioned so that about half of its length was within a wire wound resistance furnace (D). This furnace was the split type having a cylindrical heating chamber about 13 in. in length and 5 in. in diam. The front plate which supports the condenser inside the retort tube is shown as (B) in this figure. Rubber vacuum tubing (C) connected the side arm of the retort to the gas-vacuum manifold sketched in Fig. 4. This manifold accommodated a thermocouple-type vacuum gauge and valved lines leading to a mechanical vacuum pump, a mercury manometer-bubbler, a gas supply line and an air inlet. Control of pressure and composition of the gas added to the retort was obtained through manipulation of the valves on this manifold.

## PROCEDURE

The aluminum reductions of pollucite were carried out in the following manner. A weighed charge of granular aluminum metal and comminuted pollucite was thoroughly mixed, placed in a charge tray and the gross weight determined. With the retort positioned in the furnace, the loaded tray was then inserted to the rear of the retort as indicated in Fig. 2. After the front plate was secured, the system was slowly evacuated to a pressure of less than  $25 \mu$ . The controller was set to maintain a chosen temperature and the furnace power was switched on. When the



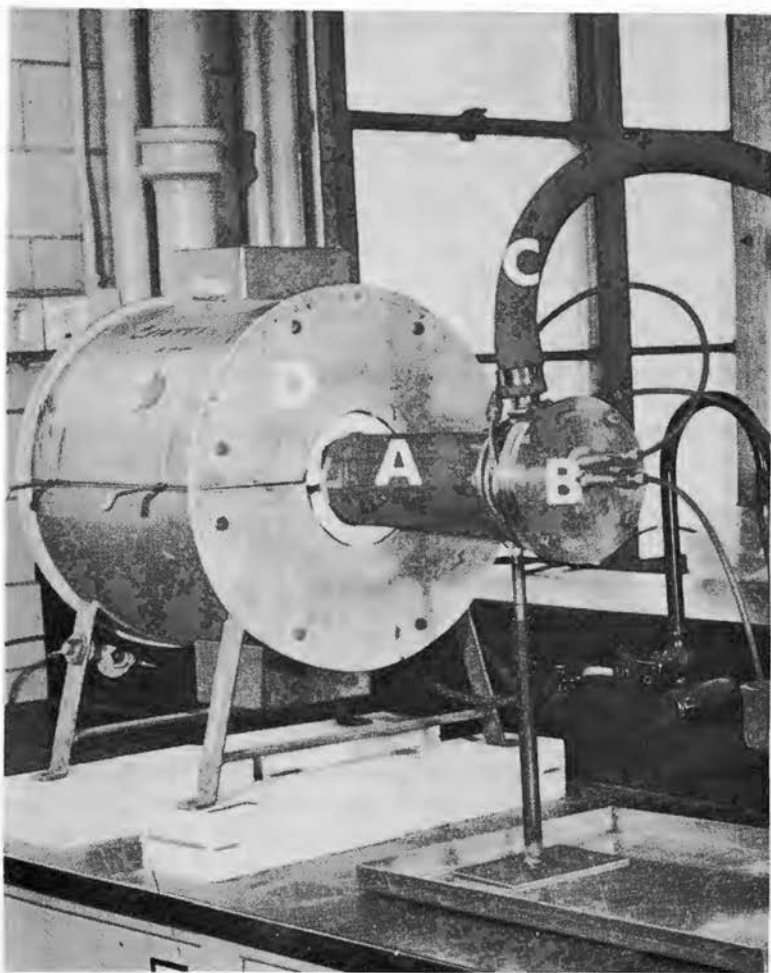


Figure 3. Retort-Furnace Assembly.

retort had heated to about  $400^{\circ}\text{C}$ , valves on the manifold were manipulated to close off the vacuum pump and to introduce a selected gas into the retort. The pressure of this gas was maintained at near that of the outside atmosphere through the mercury manometer-bubbler. Immediately following the admission of this gas, water was circulated through the cooling elements of the retort. Heating of the charged section of the retort continued until it reached the selected temperature. For example, a period of about 2 h generally was taken to heat the retort up to  $950^{\circ}\text{C}$ . The time of an experimental run was measured beginning with the time the retort attained the chosen temperature. After the experiment had proceeded for the desired length of

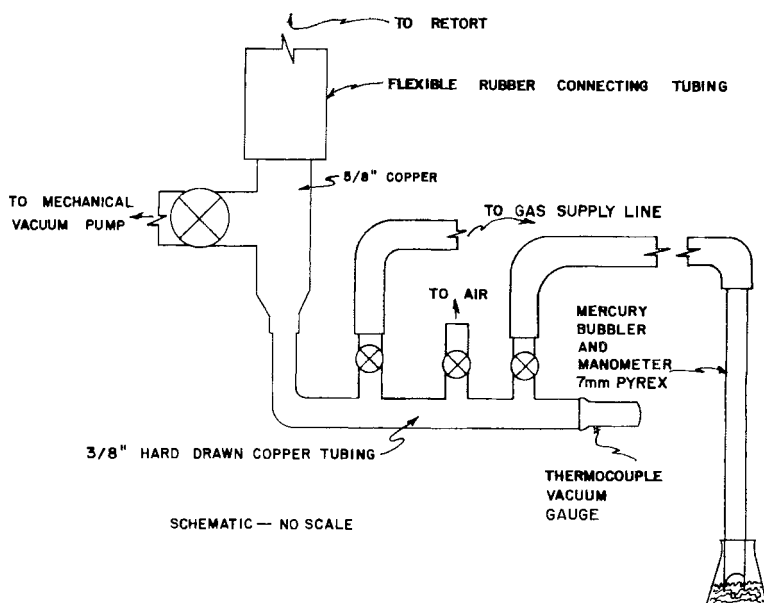


Figure 4. Sketch of gas-vacuum manifold.

time, the furnace power was switched off and the retort was cooled to below  $50^{\circ}\text{C}$ .

Since the product of this operation consists essentially of reactive alkali metals that are deposited on the water-cooled areas within the retort, caution must be exercised in recovering the tray with its residue intact and in converting the metals to compounds for quantitative evaluation. In the procedure employed here, air was first admitted into the system to facilitate partial oxidation of the crude alkali metals. The system was alternately evacuated and air admitted. After this operation, the retort was opened and the charge tray carefully removed and reweighed to determine the loss in weight during the experiment. It was observed that very little disturbance of the charge bed took place during a reduction experiment and only occasionally were detectable amounts of what could have been residue found not in the tray. The retort and front plate were cautiously sprayed with water to convert the alkali metals to hydroxides. The washings were collected in a polyethylene container; the solution was then weakly acidified with hydrochloric acid, transferred to a glass beaker and evaporated to dryness. The dry material was redissolved in a small volume of water and the resulting solution filtered. After filtration, the solution was evaporated to dryness and the product of dried chlorides was weighed and analyzed for its chemical composition.

Experiments in which no aluminum was added to the polucite ore gave blank values for the loss in weight of the ore due to temperature alone. Loss in weight of a charge during a reduction then was corrected by its blank value in order to get the corrected weight loss due to the aluminum reaction. It was found that the corrected weight loss for a charge during an experiment corresponded closely to the weight of the alkali metals in the recovered chloride product. Weight loss data were then employed in a number of cases to evaluate the dependence of yield of cesium on certain operational variables. However, in presentation of the data, the corrected weight loss is expressed as a percent of the original weight of ore in the charge.

### RESULTS AND DISCUSSION

Although the exploratory work indicated that certain conditions of operation gave promising results, the determination of optimum conditions, consistent with the particular materials and equipment chosen for the investigation, obviously required more detailed experimentation. Such factors as temperature, time at temperature, particle size of the ore, aluminum to ore ratio, compactness of the charge, amount of the charge and atmosphere needed to be investigated.

In a test to determine the effect of compactness, a charge of a mixture in pelletized form did not yield any better than the loosely packed mixture. Furthermore, it was found that when the amount of charge in the tray was varied by a factor of three, the percent yield of alkali metals remained essentially the same.

The dependence of the yield of cesium on retort temperature was investigated by first selecting, for the other possible variables, a set of conditions that appeared desirable on the basis of observations during the exploratory work. These conditions included heating at temperature for 4 h under an argon atmosphere a charge consisting of a simple mixture of 40 g of the ore, that had been ground to pass a 150 mesh sieve, and 20 g of the aluminum powder. Experiments were carried out at 50° intervals for temperatures from 800 to 1000°C, inclusively. In these experiments the weight loss, or blank, correction was approximately 0.7 g for the 40 g of ore in the charge.

In Fig. 5 a graph of the data obtained in the temperature variable experiments shows that relatively high yields of alkali metals are obtained at temperatures of 850°C and above for the Southern Rhodesia ore under the conditions specified. It is to be noted that the yield for 950°C is essentially equal to that at 1000°C and only slightly above that at 900°C.

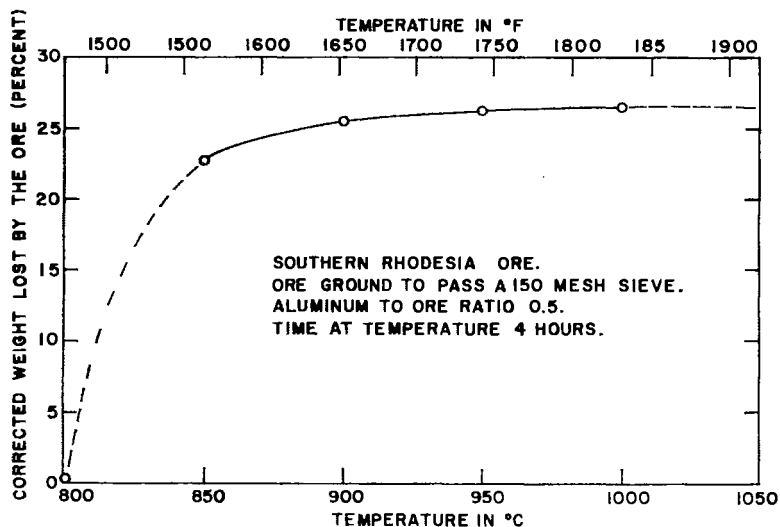


Figure 5. Yield vs temperature relationship.

A series of experiments designed to determine the relationship between time at temperature and yield were carried out for temperatures of 850°C and 950°C. The results of these experiments are presented in Fig. 6. It is to be noted that after 8 h at a temperature of 850°C the yield of alkali metals is roughly equivalent to that obtained at 950°C in only  $\frac{1}{2}$  h. Also it appears that the yield at 950°C just reaches its maximum value in 2 h under the other conditions specified.

In the experiments for Fig. 5 and 6 it is to be noted that the weight ratio of aluminum powder to ore was 0.5 or 20 g aluminum to 40 g of ore. Earlier calculations based on assumed reactions between this aluminum and the average ore indicated that the ratio of 0.35 or 35 g of this aluminum to 100 g of ore would be essentially stoichiometric. A series of experiments was set up to determine the effect of varying the ratio on the yield. Operating times of 2 and 4 h at 950°C were employed in various phases of these tests. As indicated in Fig. 7 the maximum yield appears to be obtained at about the precalculated 0.35 ratio when the charge is heated for approximately 8 h at 950°C under an argon atmosphere. However, these conditions, especially the ratio, are minima for the particular material and in order to assure adequate reaction in subsequent work with this ore a change ratio of 0.5 was employed.

The effects of various gas environments and vacuum on the yield of the metals were studied for a retort temperature of 950°C using identical charges having an aluminum to ore ratio of 0.5. The results are compiled in Table II.

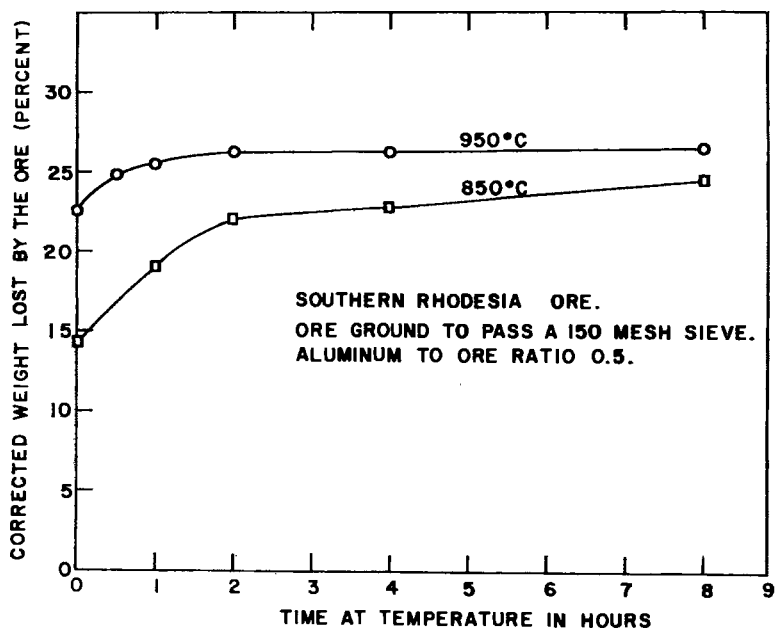


Figure 6. Yield vs time at temperature relationships.

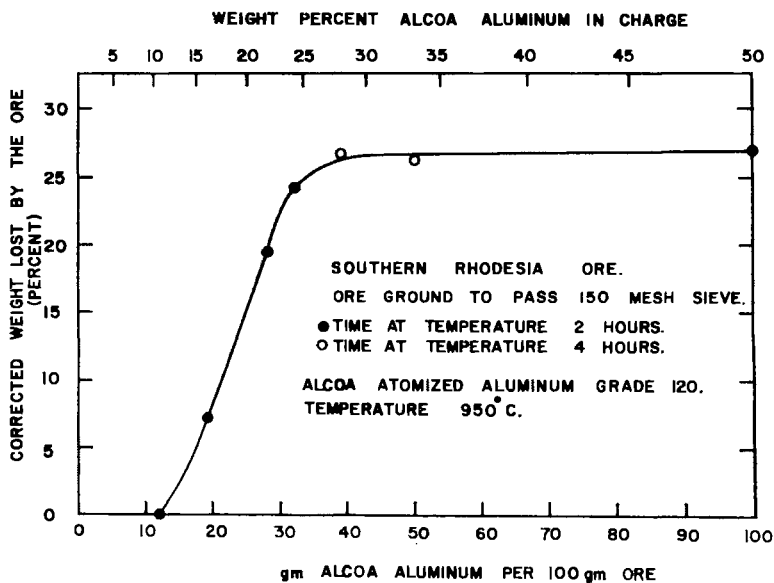


Figure 7. Yield vs composition of charge.

Table 2. Effect of atmosphere on yield of alkali metals at 950°C.

Time at Temperature	Atmosphere	Corrected wt % loss
2 h	H <sub>2</sub>	27.0 ± 0.5
2 h	He	26.3 ± 0.5
2 h	A	26.3 ± 0.5
2 h	N <sub>2</sub>	7.5
4 h	vacuum	13.0

The yields of alkali metals under hydrogen, helium and argon atmospheres are nearly equivalent and are in the range for complete removal of the alkali metals from the ore. However, the yield in a nitrogen atmosphere was down to less than one third; this drop in yield is quite likely associated with a reaction of aluminum with nitrogen rather than with the ore. In the experiment employing a vacuum, the yield was again low although the time at temperature was doubled. This effect was possibly associated with poor heat conduction in the charge but an adequate explanation of the low yield is not apparent. Although the data in the table indicate that the reduction under hydrogen is slightly better than under helium or argon, the fire hazard associated with the use of hydrogen led to the continued use of a rare gas.

In order to determine the effect of ore particle size on the reaction, a sample of as-received lump Southern Rhodesia ore was first crushed and ground to pass 20 mesh and then sieved into different ranges of particle sizes. Because the ore had minerals other than pollucite, it was possible that grinding could cause enrichment or depletion of cesium in certain size ranges. However, samples of some of the ranges were chemically analyzed and found to have essentially the same composition. Reduction experiments were then made on certain size fractions of the ore using an aluminum to ore weight ratio of 0.5 with heating at 950°C for 4 h under an argon atmosphere. The data for these tests are plotted in Fig. 8 where the yield ratio was the value of the corrected weight loss for a particular size range divided by the corrected weight loss of ore that passed a 325 mesh sieve. These data indicate that ore ground to pass a 40 mesh sieve would probably be fine enough to give appreciable reaction (at least a 0.95 yield ratio) under the conditions specified. Ore ground to pass 60 mesh would yield at least 98% of the cesium compared to ore that passed a 325 mesh sieve and likewise ore that passed a 150 mesh sieve would give a higher yield of cesium.

Since the ore that was employed in most of the experiments of this investigation passed a 150 mesh sieve, a closer evaluation of this particular grind was of interest. The ore is easily ground

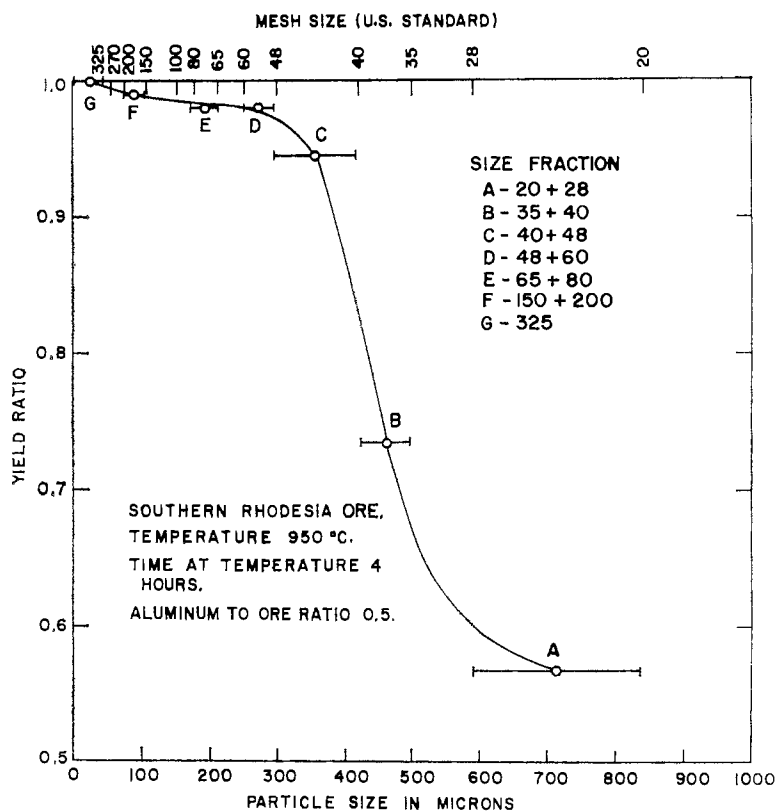


Figure 8. Yield ratio vs ore particle size.

to pass this sieve size. A particle size distribution was determined by a sieve analysis; these data are presented in Table III.

Table 3. Particle size distribution in ore ground to pass 150 sieve

Screen size passed	150	200	270	325
Percent passed	100	88	71	21

From the table, 88% of the ore is finer than the -159 +200 range plotted in Fig. 8. Almost  $\frac{3}{4}$  (71%) of this grind passed a 270 mesh sieve, so the potential yield of cesium from ore ground to pass a 150 mesh size would be well above 99% of that from ore ground to pass 325 mesh. Residues from direct aluminum reduction of ore ground to pass 150 mesh were chemically analyzed and found to contain on the average less than 0.4% of the original cesium content. The ore ground to pass 150 mesh then by difference yields better than 99.6% of the cesium. A finer grind could give a maximum gain of only 0.4% of the cesium; grinding to pass 325 mesh size or finer rather than just the 150

size then would entail some economic considerations as well as determination of operating conditions consistent with the grind.

Acceptable conditions of operation for the preparation of cesium from Southern Rhodesia pollucite ore appears to be an aluminum to ore ratio of 0.5 at 950°C for 4 h under an argon atmosphere using Alcoa Atomized Aluminum Grade 120 and the ore ground to pass a 150 mesh sieve. The metal composition of the crude product obtained by employing these conditions in a typical reduction is shown in Table IV. The data were determined by an analysis of the chloride form of the recovered metals.

Table 5. Composition of crude metal produced from Southern Phodesia pollucite reduced with aluminum.

Metal	wt %
Non-alkalies	0.3
Na	3.9
K	2.8
Rb	2.3
Cs	90.7

It is noted that the cesium content compared to the other alkalies in this metal product is higher than in the average ore composition. This result could be due to the more favorable free energy of reaction for cesium as compared to the other alkalies. However, this possible explanation has not been experimentally tested.

Because it was demonstrated that aluminum is very effective in removing cesium directly from the Southern Rhodesia pollucite, this method was tested on the pollucite ore from South Dakota. Experiments demonstrated that the South Dakota ore required a higher temperature for the aluminum to efficiently release the cesium. Furthermore, in these experiments, no exothermic reaction was observed on heating as with the Southern Rhodesia ore. An experiment in which an aluminum to ore ratio of 1.0 was employed yielded better than 99.6% of the cesium in 4 h at 1050°C under an argon atmosphere. The metal product from the ore analyzed over 93% cesium. Although a higher temperature is required with this ore, the conditions employed in this experiment were not intended to represent most desirable conditions for treating this ore.

It has been demonstrated that aluminum can effectively react with pollucite to release cesium. Operating conditions for processing a pollucite ore from Southern Rhodesia have been adopted. These conditions were found to be inadequate for treating the ore from South Dakota. An operation for processing a particular pollucite ore then would have to be designed on the



basis of experimental results for that ore. Experiments on variables such as explored in this work on the Southern Rhodesia ore could lead to the determination of operating conditions for another pollucite ore.

#### Literature Cited

- K. C. Dean, P. H. Johnson and I. L. Nichols, U. S. Bur. of Mines Rept. of Invest. RI-6387 (1964).  
 R. M. Barrer and N. McCallam, *Nature* 167, 1071 (1951).  
 R. A. Stauffer, U. S. Patent 2, 424, 512 (July 22, 1947).  
 L. Hackspill and G. Thomas, *Compt. Rend.* 230, 119-121 (1950).  
 J. Bensko, Huntsville, Alabama, Branch Research Projects Division, Physics and Astrophysics, George C. Marshall Space Flight Center (1961).  
 R. J. Moolenaar and P. R. Juckniess, U. S. Patent 3, 130, 010 (Apr. 21, 1964).  
 C. B. Hamilton, T. L. Young and H. A. Wilhelm, *Proc. Iowa Acad. Sci.* 64 (1964).  
 J. P. Coughlin, U. S. Bur. of Mines Bull. 542 (1954).

## Reactions of Thiolacids with $As_2O_3$ and $As_2S_3$ <sup>1</sup>

LYMAN R. CASWELL<sup>2</sup>

*Abstract.* Thiolbenzoic acid in refluxing benzene reacts with  $As_2O_3$  or  $As_2S_3$  to give arsenic (III) thiobenzoate. Under similar conditions dithiolterephthalic acid gives a product which appears to be  $As(SOCC_6H_4COSH)_3$ ; thioacetic acid gives acetyl sulfide; and phthaloyl sulfide is unreactive.

In the course of a series of studies of the acylation of amines (1) and of aromatic hydrocarbons by thiolacids, the hypothesis was suggested that an amphoteric sulfide, such as  $As_2S_3$ , might act on thiolacids to generate an acylcarbonium ion and a complex thio-anion, such as thioarsenite. If such an ionization occurred, the amphoteric sulfide would act as a carrier in a Friedel-Crafts acylation of benzene by the thiolacid.

When the experiment was carried out using thiolbenzoic acid and yellow  $As_2S_3$  in refluxing benzene, the product was not the predicated benzophenone, but a rose-pink compound containing sulfur, and melting, after purification, at 180-181°. This product appears to be identical with the "benzoyl thioarsenite",  $As(SOCC_6H_5)_3$ , melting at 178-179°, obtained by Rayman (2) as the result of the action of benzoyl chloride on  $As_2S_3$ .

<sup>1</sup> Grateful acknowledgment is made for the financial support of this work by the Petroleum Research Fund of the American Chemical Society and an Institutional Grant from The Texas Woman's University.

<sup>2</sup> Department of Chemistry, Texas Woman's University, Denton, Texas 76204.