The Treatment of Cesium Ore by Sulfur Chloride and Chlorine

C. B. Hamilton
Iowa State University

T. L. Young
Iowa State University

H. A. Wilhelm
Iowa State University

Let us know how access to this document benefits you

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

Literature Cited

1. Lions, Francis, Martin, Kenneth V., J. Am. Chem. Soc., 80, 3858 (1958).
2. Geldard, John F., Lions, Francis, J. Am. Chem. Soc., 84, 2262 (1962).
3. Diehl, Harvey, Wharton, H. W., J. Inorg. Nucl. Chem., 17, 120 (1961).
4. Bates, R. G., "Electrometric pH Determination", p. 117, Wiley, New York, 1954.
5. Jones, G., Bradshaw, B. C., J .Am. Chem. Soc., 55, 1780 (1933).
6. Olsen, Rodney, Diehl, Harvey, Anal. Chem., 35, 1142 (1963).

The Treatment of a Cesium Ore by Sulfur Chloride and Chlorine[1]

C. B. HAMILTON, T. L. YOUNG[2], AND H. A. WILHELM

Abstract. A Southern Rhodesian cesium ore containing essentially pollucite was chlorinated by a gaseous mixture of sulfur chloride and chlorine at temperatures between 500 and 700°C. The reaction products consisted principally of $SiCl_4$, $AlCl_3$, $CsCl$, and $CsCl \cdot AlCl_3$. Under favorable conditions for chlorination, 17 wt % of the ore remained unreacted. The optimum conditions were the fixed bed reactor used in this study were chlorination at 650°C for 4½ hr with an ore particle size that passes a 150 mesh sieve.

For a number of years cesium metal has been used as a "getter" for scavenging residual gases from vacuum tubes, as the light sensitive element in photo-electric cells, and as a reactant in certain organic syntheses. Cesium is currently receiving consideration for a number of potential applications. In the development of an ion rocket motor for deep-space propulsion systems, this metal is being tested and conditions for its use are being studied (1). Other anticipated uses for cesium are in magnetohydrodynamic and thermionic methods of power generation (1). If these applications develop as desired, the demand for the pure metal can be expected to increase sharply in atomic energy and space programs. It is estimated that a single trip of a deep-space vehicle using ion engine power will require approximately 300 lb of cesium, an amount roughly equal to the entire domestic production for the year 1962 (2). Consequently, interest in the development of new cesium production methods has increased. The work presented here deals with one aspect of the extractive metallurgy of cesium.

Bunsen and Kirchoff in 1860 discovered the element cesium by observing its spectrum in a Dürkheim mineral water (3). Twenty-one years later, Setterberg prepared the metal in Bunsen's laboratory by electrolysis of a molten salt mixture (3,4).

Pure cesium is reported to melt at 28.5°C and to boil at 670°C (5). Cesium when in the metallic state is the most reactive of any of the metallic elements derived from natural sources; special precautions are required to protect it from oxidation. Its reactivity is such that it may ignite and burn vigorously or even cause an explosion if it comes in contact with adequate air.

Cesium occurs to the extent of 3.2 ppm in the earth's crust according to Goldschmidt's estimate (6). It is the fortieth most abundant element (1) and is nearly as abundant as uranium (6). Cesium is found as a minor constituent of a variety of minerals; rhodizite and pollucite are, however, considered as the cesium minerals. Rhodizite ($Cs_2O \cdot 2Al_2O_3 \cdot 3B_2O_3 \cdot xH_2O$) is very rare; the chief commercial source of cesium is the pollucite ($2Cs_2O \cdot 2Al_2O_3 \cdot 9SiO_2 \cdot H_2O$). Pollucite was first discovered on the island of Elba, and important deposits of this ore have been found in a number of countries. The source of pollucite bearing ore used in this study was a pegmatite from the mine of Bikita Minerals (Private), Ltd. located near Fort Victoria, Southern Rhodesia.

The cost of the pure metal and its compounds are relatively high compared to the cost of the element in its ore. The current price of a pollucite ore, assaying approximately 24% cesium oxide, is $300 per ton (15c per lb.); the cesium in the ore, then, is roughly 65c per lb. The contained cesium in a technical grade cesium chloride costs nearly $40 per lb. The metal, having a purity of 99.9%, is quoted at $375 per lb at the current rate of production (7). Thus, more economical methods of extracting the cesium values from the ore and of subsequent preparation of the metal are desirable. A complete procedure for winning the pure metal from its ore would usually involve: 1) a treatment of the ore to render the cesium values water soluble, 2) processing of the soluble products to yield a purified cesium compound, and 3) preparation of cesium metal from this compound. The present study is concerned with obtaining from an ore the cesium values in water soluble form.

A common method of extracting the cesium from a pollucite type ore is to digest the finely pulverized ore with excess 6 normal hydrochloric acid at approximately 95°C for about 30 hr (8, 9, 10). This treatment yields nearly 90% of the contained cesium in soluble form. Subsequent methods of recovering the cesium from this solution may require neutralization of the acid.

In an effort to develop a more efficient and economical method of preparing cesium chloride from pollucite ore, exploratory tests were made using various chlorination procedures. Anhydrous HCl gas was passed over the ore as its temperature was increased slowly from room temperature to 800°C. There

was little evidence of reaction at any temperature in this range. A mixture of carbon tetrachloride vapors with CO_2 started chlorinating the ore at 720°C; but the reaction was slow. Higher temperatures did not appear to increase the rate of this reaction. Phosphorus trichloride was ineffective, but the pentachloride slowly chlorinated the ore at 700°C. However, the inefficiency of the process and the cost of reagent appeared prohibitive for production. The passage of chlorine over a heated mixture of carbon and ore was quite effective at 650°C. However, a test of a sulfur chloride-chlorine mixture on the heated ore gave results that warranted a more extensive study of this approach at this time. Some of the factors bearing on this treatment of pollucite ore were investigated and the results are presented in this report.

MATERIALS AND APPARATUS

The Ore

The cesium ore employed in this work was, as pointed out above, a pollucite type from a pegmatite in Southern Rhodesia. The geology of this region has been thoroughly described by several authors (11, 12, 13). In macroscopic appearance, the as-received ore is composed of pieces 1 to 4 in. in diameter which are white interlaced with small irergular purple-tinted veinlets. A published mineralogic examination of this ore lists the constituent minerals as pollucite-65%, albite-16%, lepidolite-13%, quartz-4%, petalite-1%, spodumine-1% (14). Chemical, optical, x-ray diffractometer and powder camera studies of this pollucite type ore verified the presence of pollucite, albite and lepidolite and indicated the presence of several trace minerals. A chemical analysis of the major constituents in a typical sample of the pollucite ore from this particular source gives the following percentages: Cs-25.7, Rb-1.2, Li-0.2, K-1.0, Na-1.2, A1-9.2, Si-22.7, P-0.2, O (excluding that in H_2O)-36.6, H_2O-1.9. The supplier, American Potash and Chemical Corporation, guarantees a minimum of 24% cesium oxide in the ore.

The ore was prepared for use in this study by grinding. This ore did not appear difficult to grind; however, some segregation of the minerals constituting the ore may have taken place during grinding. The purple-tinted veining material was associated with lepidolite, a lithium mica. On grinding the lepidolite tends to flake while the pollucite-rich portion pulverizes to a fine powder. In the crushing operation, the ore was first passed through a jaw crusher which reduced the size to less than ½ in. in diameter. These particles were then crushed by means of a roll mill to pass through a number 10 sieve (U. S. Standard). Further particle size reduction was accomplished with a "Mikro-Pul-

verizer," a type of hammer mill. After grinding, fractions of various particle size ranges for use in certain tests were obtained by screening.

Sulfur Chloride and Chlorine

Sulfur chloride plus chlorine as a chlorinating agent for oxides, although known for many years (15, 16, 17, 18) is not extensively used. When chlorine gas is passed over elemental sulfur at room temperature disulfur dichloride (S_2Cl_2) is formed. The liquid S_2Cl_2 first dissolves up to 66% of the unreacted sulfur (19) and further addition of chlorine converts the entire charge to S_2Cl_2. This compound is a vile smelling, yellow liquid that freezes at $-80°C$ and boils at $137°C$ (20). Further addition of chlorine to the S_2Cl_2 is assumed to give sulfur dichloride (SCl_2) which is reported to boil at $59°C$. However, according to the literature there is some question regarding the existence of simple molecular SCl_2 in the vapor state. It is generally implied that the SCl_2 decomposes on vaporization (20) setting up an equilibrium in the gas phase that may be expressed by the following reaction:

$$2SCl_2(g) \rightleftarrows S_2Cl_2(g) + Cl_2(g)$$

with most of the gas in the form of S_2Cl_2 and Cl_2. However, with excess chlorine added to the system the equilibrium most likely tends to shift the reaction toward increased SCl_2 formation.

Chlorinating Apparatus

The chlorinating apparatus employed in this investigation is represented by the sketch in Fig. 1. Two different types of glass
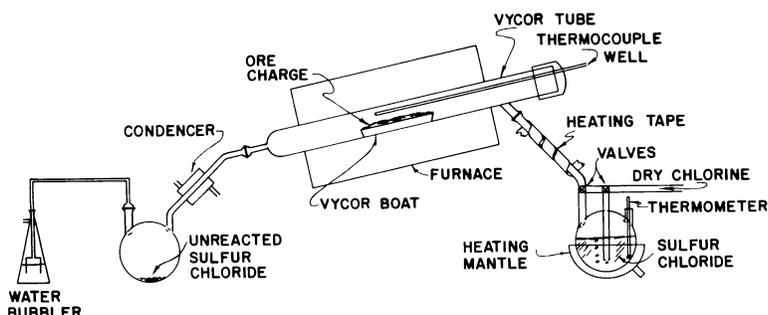

Figure 1.   Sketch of chlorination apparatus.

were employed for the complete gas train. The main section of the reaction tube which was subjected to the high temperatures of the furnace was made of Vycor tubing 30 mm in diameter. The thermocouple well was a Vycor tube sealed through the Vycor cap of the reaction tube. Pyrex ground glass joints, at-

tached to the Vycor tube by graded seals, were used to make connections with the other glass vessels. "Kel-F" No. 90 grease obtained from Minnesota Mining and Manufacturing Company was used to seal the ground glass joints and valves.

A split type furance surrounded the main reaction tube. This feature of the furance facilitated observation of the sample for short periods of time whole the reaction was taking place. Also the split type furnace permitted fast cooling when desired.

Experimental Procedure

In making a chlorination test, the cleaned reaction tube was placed in position in the furnace and a Vycor boat containing a weighed charge of ore was placed in this tube at the mid-region of the furnace. The thermocouple which was connected to a temperature-time recorder was placed in its well with the junction directly above the center of the charge.

The chlorine, at a flow rate of about 75 cc per min, was first bubbled through concentrated sulfuric acid to remove the moisture. Then it was bubbled through the liquid chloride maintained at a temperature not exceeding 65°C. The chlorine essentially saturated with the sulfur chloride flowed through the heated delivery tube to the reaction chamber. This reactive gas mixture was being passed over the charge as the furnace was heating to the desired temperature. Small amounts of ferric chloride, yellow to red in color, that deposited on the cooler walls of the reaction tube gave the first indication of chlorination of the ore. As the reaction progressed at higher temperatures, lighter colored deposits also appeared in increasing amounts in the cooler regions of the tube. Some gaseous products from the reaction passed from the furnace to the condenser.

After a period of time at the desired temperature the valves in the line were adjusted so that chlorine by-passed the sulfur chloride. The power to the furnace, heating tape and heating mantle was turned off to allow the system to cool to room temperature. Dry chlorine was passed through the system, as it cooled, in order to purge out the sulfur chloride and to prevent moisture from reaching the reaction products.

The reaction boat with the residue from the charge was removed from the tube and weighed. The residue was treated with boiling water which dissolved the soluble portion. The solution was filtered to remove the unreacted fraction which was then dried before it was weighed. The filtrate was evaporated to dryness and the salt residue from the soluble portion weighed. The soluble products that collected on the walls of the reaction tube were also treated with water. The solution thus obtained was filtered and evaporated to recover solid salts.

RESULTS AND DISCUSSION

Although the exact mechanisms by which the sulfur chloride and chlorine react with the ore are not known, the result is that chlorides of the elements are formed. At temperatures required for reaction, the chlorides of silicon and aluminum, two of the major constituents in the ore, are volatile. Pure cesium chloride, it is reported, boils at 1300°C (21); however, in the presence of aluminum chloride it appears that a more volatile double salt (possibly $CsAlCl_4$) is formed. Such a compound may account for the appreciable vaporization of cesium chloride at the lower temperatures, usually less than 700°C, employed for chlorination.

During a chlorination, the silicon tetrachloride passes as a gas from the reaction area to the water bubbler where it is hydrolyzed. The aluminum chloride is distributed along the gas train; some is retained with cesium chloride in the reaction zone, but a major portion is found in the cold exit end of the reaction tube. The cesium chloride appears to be distributed between the residue in the boat and the walls of the reaction tube. The largest fraction usually remains in the boat with any unreacted part of the charge. Most of the remainder appears as the fused double salt ($CsAlCl_4$) on the tube walls near the edge of the hot zone. A portion of the cesium chloride is carried as dust or vapor by the gas stream to the colder regions of the reactor tube.

A number of factors bear on the recovery of a soluble cesium compound from the ore. These factors include temperature of the reaction chamber, time at temperature, ore particle size, amount of ore charge, depth of fixed bed of the charge, gas composition and rate of gas flow; some have been investigated in detail. The gas composition and rate of gas flow, however, were kept at nearly constant values throughout the entire investigation. The gas composition was fixed by regulating the temperature of the sulfur chloride liquid through which the chlorine gas was bubbled. The rate of flow of chlorine was controlled by regulating its rate of bubbling through the sulfuric acid drying vessel. The size of charge (about 15 g) and the starting depth of the charge (about ½ in.) in the boat were kept fairly uniform.

The degrees of reaction obtained in tests on the sulfur chloride-chlorine treatment of pollucite ore were evaluated by determining the insoluble residues which represented the unreacted portions of the ore. Recoveries of the soluble products from the reactions were in general consistent with the determined degrees of reaction.

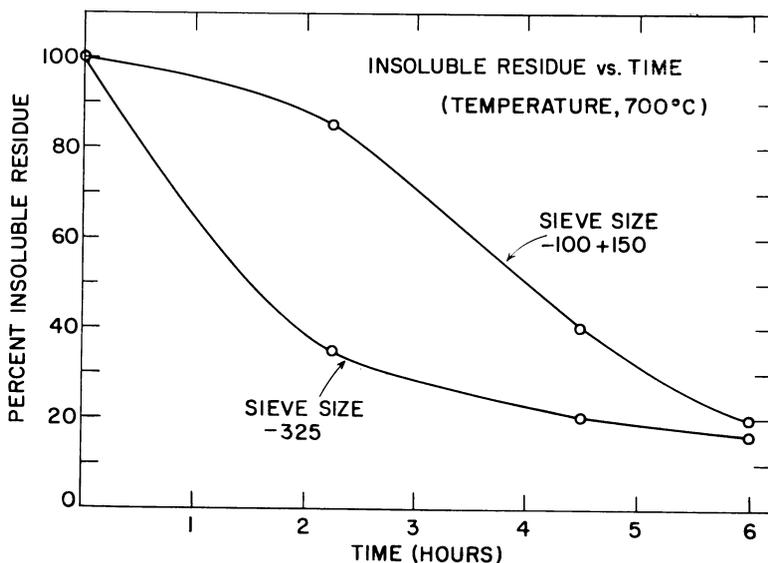The sulfur chloride and chlorine react slowly with the ore

Figure 2.   Effect of temperature and time at temperature on degree of completion of reaction.

at a temperature as low as 500°C. Figure 2 shows that after 4½ hr at 600°C the reaction is about half completed. In the same time interval at 650°C, it appears that the reaction proceeds much further; whereas, another 50° increase in temperature gives little additional effect.
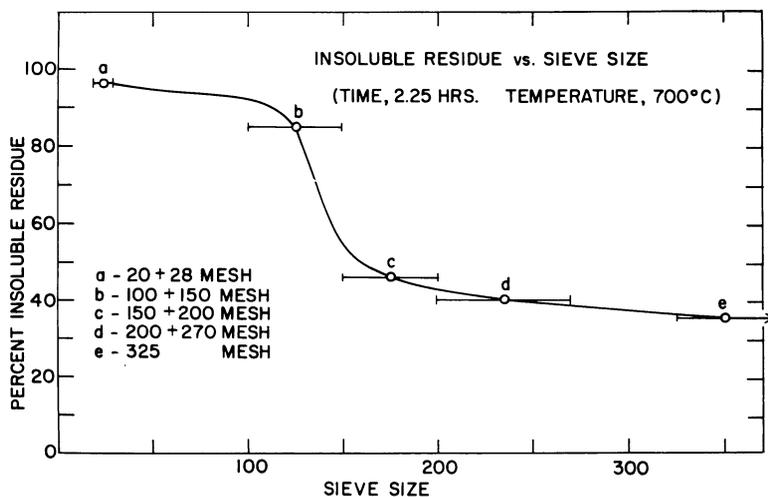

Figure 3.   Relation of particle size to degree of reaction at constant time and temperature.

It is shown in Fig. 3 that considerable advantage is gained by grinding the ore to pass through a 150-mesh sieve. However, if the reaction time is increased the larger particle sizes will eventually react to about the same extent as the smaller particle sizes. This conclusion may be drawn from inspection of the curves in Fig. 4.
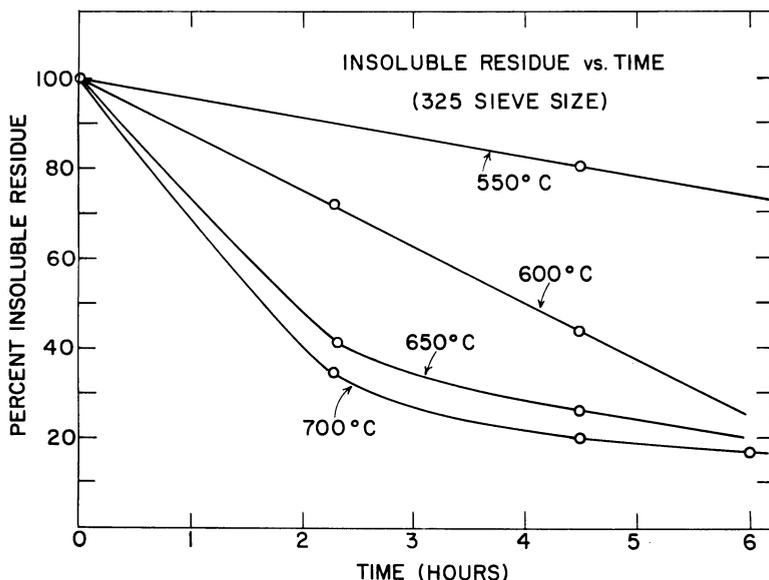

Figure 4.   Dependence of reaction on ore particle size and time at temperature.

It is to be noted in Fig. 4 that under favorable conditions for chlorination there appears to be about 17% of this pollucite ore that remains an insoluble residue. This residue when examined by x-ray diffraction exhibits the same pollucite pattern as the original ore. Chemically and spectrographically this residue contains less cesium than the starting material. The particle size distribution appears to be the same as the starting material. A charge made from the insoluble residue reacted only slightly when given the chlorination treatment a second time. The difference in reactivity of this fraction as compared to the major portion of the ore is not explained.

CONCLUSIONS

In consideration of the experimental data, it should be remembered that the ore was treated in a fixed bed type reactor. Since the reaction depends upon contact between a gas and a solid to give gaseous and solid products, much of the reaction depends on the opposing diffusion of gases into and out of a

bed of finely divided solid. It is obvious that the depth of bed is a very influential factor in determining the rate of this reaction. The plots of Figs. 2-4 were all drawn with ½ in. bed thickness and a constant flow rate. Under these conditions an effective treatment would employ a temperature of 650°C for 4½ hr using ore particles that pass through a 150-mesh sieve.

A more efficient type of reactor would have an agitated bed. If the solid particles of ore could flow counter-current to the gas stream a greater efficiency might also be realized. Any means by which the ore particles are continually mixed should effectively decrease the reaction time.

The sulfur chloride-chlorine treatment of pollucite ore appears to be a feasible method for obtaining the cesium in soluble form.

Literature Cited

1. *Rare Metals Handbook*, 2nd ed., Clifford A. Hampel, Ed. (Reinhold Pub. Corp., New York, N.Y., 1961), pp. 434-440.
2. *Minerals Yearbook* (U.S. Government Printing Office, Washington D. C., 1962) Vol. 1, pp. 1359-1360.
3. Weeks, M. E., *Discovery of the Elements*, 6th ed. (Journal of Chemical Education, Easton, Pa., 1956), pp. 626-633.
4. Carl Setterberg, Ann. Chem. 211, pp. 100-116 (1882).
5. R. J. Moolenaar, J. Metals 16, pp. 21-24 (1964).
6. V. M. Goldschmidt, *Geochemistry*, Alex Muir, Ed. (Oxford University Press, Inc., London, 1954), pp. 74-75.
7. H. A. Wilhelm and R. E. McCarley, AEC Report ISC-1029 (Rev.) (1963).
8. J. J. Kennedy, Chem. Revs. 23, pp. 157-163 (1938).
9. C. E. Berthold, J. Metals 14, pp. 355-358 (1962).
10. H. L. Wells, Am. J. Sci. 42, p. 313 (1891).
11. R. Symons, Trans. Mining and Met. 71, pp. 129-169 (1962).
12. R. Symons, J. Chamb. Mines (Rhod) 1, pp. 22-26 (1959).
13. R. Tyndale-Biscoe, Trans. Geol. Soc. S. Africa 54, pp. 11-23 (1951).
14. K. C. Dean and J. L. Nichols, U. S. Bur. Mines Rept. Invest. 5940 (1962).
15. Edgar F. Smith, J. Am. Chem. Soc. 20, pp. 289-293 (1898).
16. Roy D. Hall, J. Am. Chem. Soc. 26, pp. 1235-1250 (1904).
17. William B. Hick, J. Am. Chem. Soc. 33, pp. 1492-1496 (1911).
18. Hiram S. Lukens, J. Am. Chem. Soc. 35, pp. 1464-1469 (1913).
19. R. C. Brasted, *Comprehensive Inorganic Chemistry* (D. Van Nostrand Co., Inc., New York, N.Y., 1961), Vol. 8, pp. 92-94.
20. P. J. Durrant and Beryl Durrant, *Introduction to Advanced Inorganic*

Chemistry (John Wiley and Sons, Inc., New York, N.Y., (1962), pp. 826-827.
21. N. V. Sidgwick, *Chemical Elements and Their Compounds* (Clarendon Press, Oxford, England, 1950), Vol. 1, p. 94.

Stabilization of Lime with a Protective Glass Coating[1]

STANLEY A. LONG AND THOMAS D. MCGEE[2]

Abstract. The persistent hydration of lime has severely limited its use as a refractory material. Its hydration is somewhat retarded, but not prevented by heat treatment. A number of investigators have attempted to stabilize lime with chemical additions and have met with limited success. In this investigation an attempt has been made to stabilize lime by introducing a protective coating of glass and by hot pressing to reduce the porosity. Powdered refractory glasses and granular lime were hot pressed in a graphite mold at temperatures ranging from 1250 to 1450°C. The glasses were: 1) calcium-aluminate, 2) alumino-silicate and 3) alumino-phosphate. Samples pressed with the alumino-silicate glass showed poor bonding and disintegrated when removed from the mold. Samples made with the calcium-aluminate and the alumino-phosphate glass showed good resistance to hydration when exposed to the atmosphere. Samples pressed with the calcium-aluminate glass at 1450°C withstood immersion in water at room temperature for 72 hours without disintegration.

Calcium oxide, or quicklime, has a melting point of 2572°C. Next to magnesite, it is the most refractory commercial oxide (11). Unlike magnesite, it is widely distributed in deposits of great purity (limestone). If these were the only considerations, CaO refractories would be valuable for a number of applications. However, little success has been had with this material as a refractory, for it hydrates readily in both air and water. This hydration results in a large volume increase and in the disintegration of any CaO article.

The hydration tendency of CaO decreases with increasing firing temperature, but no matter how it is heat treated it is impossible to convert it to a stable form (13). Lime which has been heated below 1000°C reacts with water immediately to form $Ca(OH)_2$ with the evolution of a large amount of heat, while lime burnt at a higher temperature reacts more slowly. A lump of crystalline lime placed in water is dissolved very slowly at the surface, the hydration being so gradual that there is no apparent rise in temperature. There is no change in the