**AMES
LABORATORY
IOWA STATE
COLLEGE**

ENGINEERING . QUARTERLY SUMMARY RESEARCH REPORT .
APRIL, MAY, JUNE, - 1955.

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U N C L A S S I F I E D

ISC-642

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

QUARTERLY SUMMARY RESEARCH REPORT IN ENGINEERING

For April, May, June 1955

by

Ames Laboratory Staff

November 23, 1955

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng 82

U N C L A S S I F I E D

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QUARTERLY SUMMARY RESEARCH REPORT IN ENGINEERING

For the period April, May, June 1955

This report is prepared from material
submitted by group leaders of
the Laboratory

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ENGINEERING

Under the direction of F. H. Spedding, G. H. Beyer,
G. L. Bridger, R. W. Fahien, R. W. Fisher, G. Murphy and
M. Smutz

Chemical Engineering1. Processing of Monazite Sands (M. Smutz)*

A report (ISC-662) entitled "Thorium and Uranium from Monazite" by Martin Welt and Morton Smutz will be distributed.

Work continues in the study of alternate methods of processing monazite sands for the recovery of thorium, uranium and the rare earths. In this work the first step is a sulfuric acid digestion of the sands followed by dissolution of the digested mass in cold water. The next step is an oxalic acid precipitation of the thorium and rare earths leaving the uranium in solution. The uranium is then extracted from the aqueous solution with a variety of solvents. The thorium is separated from the rare earths by calcining the oxalates to the oxides, dissolving the oxides in nitric acid and extracting with tributyl phosphate. The cerium can be removed along with the thorium by oxidizing the cerium to the ceric state. It was found that by selective stripping the thorium can be separated from the cerium.

An evaluation of these alternate processing methods is now in progress.

2. Uranium from Phosphates (G. L. Bridger)

One phase of the project on recovering uranium from normal superphosphate was completed. This work is summarized in ISC-612.

ABSTRACT

Florida phosphate rock and the phosphoria formations of Idaho, Montana, Utah and Wyoming have a uranium content ranging from 0.01 to 0.02 per cent. The abundant domestic reserves and the relatively large tonnages of phosphate rock mined each year cause

*Names indicate group leaders in charge of work.

these low-grade uranium sources to be of great potential importance. Most phosphate rock is used for the production of normal superphosphate, which is made by acidulating the rock with sulfuric acid to get a form of phosphorus available to plant life. This study was undertaken to develop a method of recovering uranium during the production of superphosphate without destroying the plant nutrient value of the product.

A process was developed that is capable of recovering at least half of the uranium present in superphosphate. The process consists of a single step liquid-slurry extraction in which an organic solvent is mixed with freshly acidulated phosphate rock. A solution of 10 per cent octyl pyrophosphoric acid in kerosene is used as the solvent. A 10 minute extraction with as little as 0.24 lb. of this solvent per lb. of rock was capable of recovering uranium.

Two different acidulation-extraction procedures were studied. The first of these used an acidulation of 1.81 lb. of sulfuric acid per lb. of rock P_2O_5 . This corresponds to the acidulation used commercially to prepare superphosphate. With this process, the solvent was mixed with the acidulated rock slurry and then the phases were separated. There was never a clear aqueous layer present during the extraction when acids of concentration higher than 60 per cent were used. The other procedure that was studied used an initial acidulation of 2.50 lb. sulfuric acid per lb. of rock P_2O_5 . This is the acidulation commonly used to produce wet process phosphoric acid. The solvent was mixed with the over-acidulated rock and then the phases were separated. When this process was used, the aqueous phase separated into two layers, a slurry of acidulated rock on the bottom and a clear liquid above. After the solvent was removed, sufficient additional phosphate rock was added to the aqueous phase to reduce the overall acidulation to 1.81 lb. sulfuric acid per lb. of P_2O_5 . Superphosphate was obtained as the final product. The maximum uranium recovery obtained by either method was about 50 per cent of that present in the acidulated rock.

A considerable amount of solvent was occluded by the freshly acidulated rock. The samples prepared in the laboratory were filtered and washed with kerosene but even with vacuum filtration some organic was still held by the fresh superphosphate. It was

concluded that a drying operation would be necessary to completely remove the organic materials. Kerosene has too high of a boiling range to be removed by drying. A lower boiling material such as n-heptane would have to be used. The quick-cure process for production of superphosphate uses a drying operation to cure the material. A similar process could be used to simultaneously cure the superphosphate and remove organic materials.

The uranium recovery seemed to be limited mainly by two factors. One of these was the extent of apatite lattice destruction by the sulfuric acid. This was measured by P_2O_5 conversion. Only uranium freed from the apatite lattice can be recovered by solvent extraction. The other limiting factor was the possible formation of UF_4 during the acidulation of the rock. Uranium tetrafluoride is insoluble in octyl pyrophosphoric acid. The use of oxidizing agents, which may have formed U^{+6} thereby preventing the formation of UF_4 , during the acidulation had a beneficial effect on uranium recovery.

Although the maximum uranium recovery obtained was only half of that present in the acidulated rock, it still represents a domestic source of approximately 500 tons of uranium annually. A raw material cost study indicated that an acidulation-extraction process may be economically feasible if the octyl pyrophosphoric acid and diluent could be recovered from the superphosphate. It was concluded that the process warranted further study to determine operating costs and to determine if uranium recovery can be increased.

3. Zirconium Process Development (G. H. Beyer)

A report (ISC-634) entitled "Conversion of Zirconium Sulfates to Anhydrous Zirconium Tetrafluoride" by G. H. Beyer, E. L. Koerner and E. H. Olson was distributed.

ABSTRACT

Increased interest in zirconium metal has resulted in attempts to develop cheaper processes for winning zirconium from its domestic ore zircon. One such process, now under development at the Ames Laboratory, consists of opening up zircon sand

by caustic fusion and dehydrating the silica by sulfuric acid dissolution. Crystals of zirconium sulfate are then reacted with 70 per cent hydrofluoric acid to form hydrated zirconium fluoride, which is dried at elevated temperatures under an atmosphere of anhydrous hydrogen fluoride. Anhydrous zirconium tetrafluoride can be bomb-reduced with calcium to yield ductile zirconium metal.

This report discusses production of zirconium tetrafluoride suitable for making soft zirconium metal. The quality of the zirconium metal was dependent upon the purity of the fluoride employed in the reduction. Particular emphasis was placed upon the preparation of zirconium sulfate and pentazirconium disulfate, since the major portion of the impurities had to be removed in this step in order to produce a high-purity fluoride.

The dehydration of zirconium tetrafluoride monohydrate was studied. Satisfactory dehydration conditions resulted when the fluoride was heated at 400°C. for four hours under an anhydrous hydrogen fluoride atmosphere. Sulfate contamination in the form of unconverted zirconium sulfate caused caking in the dehydration step and increased conversion time. Hydrated zirconium tetrafluoride free from sulfate contamination was prepared from pentazirconium disulfate. Because the disulfate also resulted in a granular fluoride, it was the preferred sulfate for making the fluoride. Sodium fluoride contamination was found in zirconium tetrafluoride prepared from pentazirconium disulfate. However, this sodium fluoride was not detrimental to the quality of the metal because it was removed in the slag of the bomb reduction.

The investigation showed that zirconium sulfate tetrahydrate and pentazirconium disulfate can be satisfactorily converted to zirconium tetrafluoride. The quality of the zirconium metal produced was sufficiently soft (Rockwell A hardness 43-46) to indicate that sulfate contamination can be controlled.

Ceramic Engineering

1. Metal-Ceramic Reactions (M. Smutz and G. R. Pulliam)

The purpose of this investigation is to study the reaction of cerium and lanthanum metals in contact with refractory oxides. The study also includes determination of surface tension and work of adhesion of the metals in contact with the ceramics. A study is being made of the interfacial reactions occurring by metallographic and x-ray diffraction techniques.

Two determinations of surface tension of cerium metal on BeO gave average values of 745 $\frac{\text{dynes}}{\text{cm}}$ within the precision of the experiment, $\pm 5\%$. The average value obtained from two determinations on ZrO_2 was 700 dynes/cm.

Measurements of the surface tension of lanthanum on ZrO_2 yielded an average value of 710 dynes/cm.

2. Refractory Characteristics of Molybdenum Disilicide (M. Smutz and D. Wilder).

A study has been completed concerning the grain growth phenomena observed in sintering molybdenum disilicide. Particular attention to iron contamination has shown this element to be a strong contributing factor in the promotion of growth. In view of this considerable influence on the microstructure and also the observed creep in iron contaminant material, which decreases the usable temperature of molybdenum disilicide, a study of the creep properties of this material has been initiated.

Other Engineering Research

1. Circulation of Molten Metals (R. W. Fisher)

The bismuth-uranium alloy molten metal loop is continuing to operate satisfactorily at the range of 950°C . This loop has now been running for over 2800 hours, which is quite indicative that the tantalum is a suitable material for containing such an alloy. A thief sample was taken of the alloy after 2000 hours and analyzed spectrographically and chemically. It was found that only 5 ppm tantalum was present in this sample, confirming our belief that the tantalum does not react in the presence of this uranium-bismuth fuel. We are continuing to operate this loop until such time as we receive a radiation source adequate to x-ray the equipment.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-531 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. July, August, September, 1954.
- ISC-574 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-576 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-577 Ames Laboratory Staff. Physics, Quarterly Summary Research Report. October, November, December, 1954.
- ISC-598 W. A. Rhinehart and D. J. Zaffarano. A Voltage Calibration System for Accurate Pulse Height Measurement.
- ISC-599 R. A. Lowry, J. E. Osher and G. H. Miller. A Pressure Regulator for a Low Pressure Continuous Flow Ionization Chamber.
- ISC-601 R. W. Fisher. Comprehensive Report on Production of Thorium IA. Thorium Fluoride Preparation.
- ISC-602 R. N. Kniseley and V. A. Fassel. A Rotating Step Sector for Use with AC or Other Intermittent Spectrographic Light Sources.

2. Papers Published in Scientific Journals

- Banks, C. V. and R. J. Davis
Analytical Applications of the Reaction of Thorium with Benzenephosphoric Acid. Anal. Chem. Acta 12, 418-31, (May, 1955).
- Banks, C. V. and R. E. Edwards. Separation and Determination of Thorium and Aluminum. Anal. Chem. 27, 947-49 (June, 1955).
- Dooley, M. E. and D. F. Atkins
A New Electronic Vacuum Dilatometer. Rev. Sci. Instr., 26, 568-71 (June, 1955).
- Duke, F. R. and R. W. Laity
The Measurement of Transport Numbers in Pure Fused Salts. J. Phys. Chem., 59, 549-52 (June, 1955)
- Duke, F. R. and F. R. Parchen
Kinetics of the Reduction of Ferric Ion by Hydroquinone in the Presence of 1,10-Phenanthroline. J. Am. Chem. Soc. 77, 3198-99 (June, 1955).

- Fassel, V. A., B. Quinney, L. C. Krotz and C. F. Lentz
Quantitative Spectrographic Analysis of the Rare Earth
Elements. Anal. Chem., 27, 1010-14 (June, 1955).
- Fassel, V. A. and H. J. Hettel
Isotopic Assay of Lithium by Means of Hydride Band
Emission Spectra. Spectrochim. Acta, 7, #3, 175-78
(May-June, 1955)
- Grantham, L. F., T. S. Elleman and D. S. Martin, Jr.
Exchange of Chlorine in Aqueous Systems Containing
Chloride and Tetrachloroplatinate. II. J. Am. Chem.
Soc., 77, 2965-71 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron Beam
in a Conventional Synchrotron. Rev. Sci. Instr., 26,
594-98 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron
Beam in a Conventional Synchrotron. II. Rev. Sci.
Instr., 26, 598-600 (June, 1955).
- Hansen, R. S. and R. D. Hansen
The Adsorption of Hydrocarbons for Menthanol and Ethanol
Solutions by Non-Porous Carbons. J. Phys. Chem., 59,
496-498 (June, 1955).
- Hansen, R. S., F. A. Miller and S. D. Christian
Activity Coefficients of Components in the System Water-
Acetic Acid, Water-Propionic Acid, and Water-n-Butyric
Acid at 25°C. J. Phys. Chem., 59, 391-95 (May, 1955).
- Hughes, F. J. and D. S. Martin, Jr.
Kinetics of the Oxidation of Selenious Acid by Hydrogen
Peroxide. J. Phys. Chem., 59, 410-15 (May, 1955).
- Klingman, D. W., D. T. Hooker and C. V. Banks
Photometric Titration Assembly for Beckman Model DU
Spectrophotometer. Anal. Chem., 27, 572 (April, 1955).
- Nadler, M. R. and E. S. Fitzsimmons
Preparation and Properties of Calcium Zirconate. J.
Am. Ceram. Soc., 38, 214-17 (June, 1955).
- Nichols, R. T., A. V. Pohm, J. H. Talboy, Jr. and E. N. Jensen
A Beta-Ray Spectrometer for Coincidence Measurements.
Rev. Sci. Instr., 26, 580-83 (June, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Mallinckrodt Chemical Works 3600 North 2nd Street St. Louis, Missouri	50 mg thulium oxide 50 mg lutetium oxide
Dr. Daniel Laszlo, Chief Div. of Neoplastic Diseases Montefiora Hospital New York 67, N. Y.	25 gm yttrium oxide 99.9%
Dr. S. Jaffe Air Reduction Co., Inc. Research Laboratory Murray Hill, New Jersey	2 gm pure thulium oxide
U. S. Bureau of Mines Rare and Precious Metals Experiment Station Reno, Nevada	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 1 gm erbium oxide 1 gm ytterbium oxide 100 mg holmium oxide 100 mg thulium oxide 100 mg lutetium oxide 100 mg terbium oxide
Dr. Charles E. Holley, Jr. Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm yttrium metal 20 gm dysprosium metal 20 gm erbium metal 20 gm ytterbium metal
Brookhaven National Laboratory Upton, Long Island, New York	50 gm cerium metal
Supply Officer Naval Research Laboratory Washington, D. C.	100 gm thorium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	100 gm ytterbium oxide 100 gm erbium oxide 100 gm dysprosium oxide
Litton Industries Beverly Hills, California	3 thulium buttons

<u>Destination</u>	<u>Item</u>
Dr. LeRoy Eyring Department of Chemistry State University of Iowa Iowa City, Iowa	20 gm lanthanum oxide 20 gm cerium oxide 20 gm neodymium oxide 20 gm praseodymium oxide 20 gm samarium oxide 20 gm ytterbium oxide 10 gm gadolinium oxide 5 gm terbium oxide 5 gm thulium oxide
General Electric Co. A. N. P. Department Cincinnati, Ohio	30 gm yttrium oxide 50 lb yttrium oxide (Highest purity) 1 lb samarium metal 10 lb yttrium metal 1 lb gadolinium metal
Dr. Howard E. Kremers Lindsay Chemical Co. West Chicago, Illinois	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Supply Officer Naval Research Laboratory Washington 25, D. C.	0.5 gm erbium metal 0.5 gm dysprosium metal
Research Laboratories of Colorado, Inc. Newtown, Ohio	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide

<u>Destination</u>	<u>Item</u>
Battelle Memorial Institute Columbus, Ohio	2 gm neodymium oxide 2 gm gadolinium oxide
State University of Iowa Purchasing Department Iowa City, Iowa	5 gm lanthanum metal 5 gm praseodymium metal 5 gm samarium metal 5 gm ytterbium metal
Trans World Airlines, Inc. Kansas City 15, Kansas	2 thulium buttons
M. I. T. Lincoln Laboratory Lexington, Massachusetts	1 gm gadolinium metal 1 gm dysprosium metal 1 gm erbium metal
Argonne National Laboratory Lemont, Illinois	30 mg thulium oxide 30 mg holmium oxide
Dr. Paul V. Harper Chicago, Illinois	20 gm yttrium oxide 99.8%
Dr. Nathan Sugarman Chicago, Illinois	2 gm praseodymium metal 2 gm holmium metal
National Bureau of Standards Washington, D. C.	1 lb lanthanum metal 1 lb cerium metal
Mallinckrodt Chemical Works 65 Destrehan Street St. Louis, Missouri	50 mg terbium oxide 50 mg dysprosium oxide 50 mg erbium oxide 50 mg lutetium oxide 50 mg thulium oxide
Argonne National Laboratory Lemont, Illinois	1 sample samarium metal 1 sample neodymium metal
Commanding Officer U. S. Naval Hospital St. Albans, New York	5 gm Y ₂ O ₃ 99.9%
Florida State University Tallahassee, Florida	2 gm ytterbium oxide
Carbide and Carbon Chemicals Co. X-10 Plant Oak Ridge, Tennessee	200 gm erbium oxide 500 gm neodymium oxide 200 gm holmium oxide 400 gm yttrium oxide 400 gm neodymium oxide
American Metallurgical Prod. Co. New Castle, Pennsylvania	1 lb lanthanum metal (99% pure)