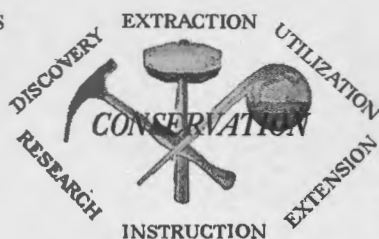


College of Mineral Industries



The  
Pennsylvania State University

UNIVERSITY PARK, PA., MAY 1958

## Chemical Beneficiation Grows in Importance\*

H. B. CHARMBURY† and J. W. LEONARD‡

The methods used to concentrate or beneficiate an ore may be divided into three general categories: (1) those based upon the differences in specific gravity of the minerals; (2) those based upon the differences in the electrical properties; and (3) those based upon differences in the chemical properties. Although economics dictate that the first two methods be used whenever possible, the third method has become of great industrial importance in recent years and in all probability will continue to increase in importance.

There are two major reasons for the growing importance of chemical beneficiation: (1) tremendous consumption of the more common minerals has forced the mining of increasingly leaner ores; and (2) recent advances in science and technology have created a demand for the less common minerals which occur in their ores in extremely low concentrations. Both of the above reasons share in common the ever increasing problem of low grade. The cheaper, non-chemical methods of beneficiation are ruled out for many low-grade ores because the extreme fine size of the particles make their liberation difficult and sometimes virtually impossible.

The classic example of the lean ore problem exists in the iron mining industry. To be acceptable for the blast furnace iron ore should contain about 50% iron. For many years this was no problem. The original ore could simply be mined and shipped directly to the steel mills. However, this type of ore is now available in this country only in limited amounts; therefore, it is necessary to use an increasing amount of lean taconites, containing around 27% iron. This, of course, requires beneficiation to improve the grade to a minimum 50% iron. The magnetic taconites are concentrated electrically, while the nonmagnetic forms have been beneficiated by chemical flotation.

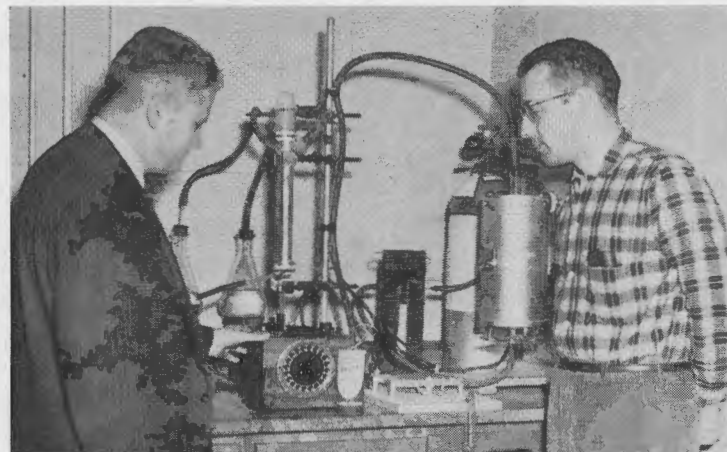
Other examples of lean ores are the copper ores which are often upgraded from less than 1% copper to 15-17% copper to be acceptable to the smelter. Uranium ores with as little as .015%  $U_3O_8$  and tungsten ores with as little as .017%  $WO_3$  are being considered for processing. In each instance, this is less than 0.3 of a pound of the element per ton of ore.

\* Based upon a paper presented by H. B. Charmbury before the South-eastern Pennsylvania Section of the American Chemical Society at Gettysburg College, Gettysburg, Pa.

† Professor and Head, Department of Mineral Preparation.

‡ Research Assistant, Department of Mineral Preparation.

(Continued on page 4)



Dr. Charmbury left, and Mr. Leonard, right, examining the apparatus used to study the chemical beneficiation of low-grade Pennsylvania iron bearing sandstone.

## The Pennsylvania Silica Brick Industry - An Enigma

M. SHEINKIN,\* H. L. LOVELL,† and H. B. CHARMBURY‡

The Pennsylvania silica brick industry has been a leader for many years in providing the country with quality products for the metallurgical industry. Pennsylvania's declining role (Table I and Table II) in recent years has been associated with the changing requirements in the alumina content of the silica brick. To meet these requirements the industry has had to import silica from Ohio, New Jersey, and Maryland. In adjusting to meet the new specifications, costs have increased to such an extent that Pennsylvania plants may be forced to relocate in other states. A means of retaining those plants in the Commonwealth may be found, however, through a well-planned research program on the mineral preparation problems involved.

Larger quantities of silica brick are used than any other refractory except fire clay. In the 16,000 by-product coke ovens in the United States and Canada, 65 per cent of the brick used is made of silica.<sup>1</sup> Although coke oven linings and other metallurgical furnace applications are important users of silica brick, open hearth furnace requirements are larger and more critical. Such refractories form the roofs of these furnaces and amount to about one third of the bricks employed. The open hearths have campaigns (life expectancies) varying from 50 to over 300 heats. The length of the campaign, and thus the cost factor, is directly related to the

\* Graduate Assistant, † Assistant Professor of Mineral Sciences, and ‡ Professor and Head, Department of Mineral Preparation.

(Continued on page 2)

# Mineral Industries

Published Monthly  
from October to June, inclusive  
by

THE PENNSYLVANIA STATE UNIVERSITY  
COLLEGE OF MINERAL INDUSTRIES  
MINERAL INDUSTRIES EXTENSION SERVICES

D. C. JONES, *Director*

JEANNE L. SLOBOD, *Editor*

## PENNSYLVANIA'S COLLEGE OF MINERAL INDUSTRIES

### Dedicated to

Instruction and research in all fields of mineral discovery, extraction, and utilization to the end that true conservation — the efficient exploitation of known mineral deposits, the discovery of new deposits, and the development of new techniques for using mineral raw materials not now industrially employed — shall be achieved now and in the future.

### DIVISIONS OF SERVICE

EARTH SCIENCES: Geology, Mineralogy, Geography, Geophysics, Geochemistry, and Meteorology.

MINERAL ENGINEERING: Mining Engineering, Mineral Preparation Engineering, Petroleum and Natural Gas Engineering, and Mineral Economics.

MINERAL TECHNOLOGY: Metallurgy, Ceramic Technology, and Fuel Technology.

### FIELDS OF WORK

Resident Instruction  
Research  
Extension Instruction  
Correspondence Instruction

Entered as second-class matter at State College, Pa., November 1, 1938, under the Act of August 24, 1912.

MAY 1958

## Coal Workshop Held in April

"MOTIVATING FOR GREATER EFFICIENCY" was the theme of a workshop for the upper management levels of the coal industry sponsored by The Pennsylvania State University and held March 30 through April 4 at the White Sulphur Springs Hotel at Mann's Choice, Pennsylvania, near Bedford. The workshop, the second annual one to be held for coal industry management executives, was coordinated by R. B. Hewes, professor of Mineral Industries Extension, and O. H. Tribble of Penn State.

## Petroleum Short Course Planned

A SHORT COURSE in petroleum reservoir engineering will be held on the campus May 26 through June 13.

The first part of the course will deal with the properties of reservoir fluids, porous media, and fluid flow. This material will serve as a refresher for practicing petroleum engineers and will provide the necessary background for those new to the field.

The larger portion of the three-week course will deal with the actual computations involved in the handling of reservoir problems, with emphasis on an understanding of the methods and their applicability and limitations.

## PENNSYLVANIA SILICA BRICK INDUSTRY

(Continued from page 1)

silica brick roof life. The cost of silica refractories in steel production is approximately \$2.00 per ton of steel. The useful maximum temperature of such refractories (3060°F; 1682°C) is within 10-90°F (6-50°C) of their melting temperature and places an upper limit on the temperature of the steel-making process which requires a 2820-2910°F (1549-1599°C) minimum tapping temperature.\* The economic requirements of the steel industry favor higher temperatures and more vigorous furnace usage, and consequently there is a need for stronger, more refractory bricks which will give a longer roof life. The accompanying photograph illustrates a silica brick failure in a small electric arc furnace showing that enough spalling and melting has occurred to contaminate the melt.

Among the factors which determine roof life of the brick is the alumina content. Although pure silica melts at 3135°F (1723°C), the temperature of partial melting drops rapidly with even small additions of alumina, titania, and the alkalies, which in turn makes roof failure more likely. Conventional silica brick containing 0.5 per cent  $Al_2O_3$  fails under a 25 pound per square inch load at 2975-3025°F (1638-1663°C), while super-duty brick with 0.3 per cent  $Al_2O_3$  will withstand this load at temperatures to 3060-3080°F (1682-1693°C). The use of brick with these strength-temperature characteristics reduces the cost per product ton of steel; silica brick specifications, therefore, have been changed from 1.0 per cent maximum alumina to less than 0.3 per cent for super-duty brick.

The Pennsylvania silica brick industry is represented by a dozen small plants located near huge deposits of Tuscarora (Medina) or Chickies quartzite. These large quartzite deposits have barely been opened so that very large reserves exist. More recently, areas of the Oriskany conglomerate containing silica pebbles of low alumina content have been employed. The pebbles in the Oriskany are expected to provide brick raw materials for at least forty years.

The Tuscarora sandstone contains from 0.5 to 5.0 per cent  $Al_2O_3$  and the following analysis is typical:<sup>3</sup>

$SiO_2$	95.67%
$Fe_2O_3$	0.59
$Al_2O_3$	0.92
CaO	2.24
MgO	0.27

The prepared Oriskany pebbles contain about 99 per cent silica, 0.2 per cent alumina, 0.2 per cent iron oxide, and trace amounts of alkalies, calcia, magnesia, and titania.

The industry has sought to meet the more stringent requirements in alumina content by several steps: 1) crushing and grinding have been augmented by simple washing processes to reduce liberated surface impurities, thus providing a raw material near the 1.0 per cent alumina level; 2) blending of local stone with transported higher-grade ganister from other Pennsylvania quarries and pebble deposits or with high-grade pebbles from Ohio, to yield a product meeting specifications; and, finally the current practice, 3) importing all plant raw materials of high purity. These adjustments increase costs and tend to force Pennsylvania plants to relocate in other states. At least one new plant has already been constructed out of state because of this problem. As a further result, Pennsylvania ganister quarry operations at Tipton, Port Matilda, Julian, Mount Union, and Womelsdorf are now idle. The labor force, although not large, represents an important economic factor in a number of Pennsylvania communities.

The increased market for low alumina silica brick has not yet caused a depletion of high-quality materials country-wide, but maintaining a supply of suitable raw materials within the Commonwealth necessitates the application of mineral beneficiation processes to the problem of reducing the alumina content of local reserves. If Pennsylvania silica brick makers must import pebbles from Ohio, the costs of such pebbles are high enough to offer some encouragement that mineral beneficiation of local high-silica raw materials may be cheaper and at least as satisfactory. The cost of purchase and transport of Ohio pebbles to Pennsylvania plants is \$3.71 per ton from Eastern Ohio to Central Pennsylvania. The fraction of this amount, then, chargeable as freight for pebbles from Ohio to the Pennsylvania plant is the amount the Pennsylvania silica brick manufacturer can spend on beneficiation of his local raw materials. Although the tonnage used in making silica brick is large, processes not applicable to massive quantities may be considered because of the low value applied to the original stone.

Since, as has been shown, alumina content exerts a profound control on service life, it is fortunate that techniques can be developed which will permit a considerable

TABLE I  
Ganister Production\*

YEAR	UNITED STATES Tons	Tons	PENNSYLVANIA	
			% OF TOTAL U. S.	NET VALUE (\$/TON)
1916	859,956	675,424	79	0.61
1920	1,095,390	761,750	70	1.48
1925	756,630	579,950	77	1.21
1930	718,370	483,160	67	1.24
1935	525,000	318,140	61	1.26
1941	1,236,370	697,520	56	1.75
1945	1,480,740	1,024,030	69	1.82
1950	1,102,280	607,030	55	3.96
1951	1,223,299	723,102	58	4.78
1952	.....	676,885	....	4.72
1953	1,152,912	588,583	51	5.91
1954	.....	496,848	....	4.53

\* U. S. Bureau of Mines Minerals Yearbooks

significant removal of alumina from Pennsylvania raw materials.

The technological situation to be met by beneficiation methods, however, is formidable and contradictory. Most ganister is characterized by small angular quartz grains of high purity cemented by thin films and pockets of clay and other silicates containing varying amounts of alumina, iron oxides, titania, and carbonates. The industry is not optimistic regarding beneficiation possibilities because of the physical relations and chemical combinations between the silica particles and impurities. The removal of the impurities is possible only upon their liberation from the quartz particles. A sufficient degree of liberation is not attained by size reduction alone, although removal of extreme fines (-200 mesh) does reduce the alumina content because the impurities tend to be fine-grained. Any beneficiation-directed comminution creates difficulties in attaining product size-consist specifications. These size requirements, however, must be met and cannot be appreciably altered if the necessary brick permeability-porosity properties are to be obtained.

The density and particle size relationships between the clay impurities and the silica particles are not favorable for gravity separations. Nor do the chemical reactivities favor simple hydrometallurgical separations.

Evidence indicates that perhaps blending of mine run material with a beneficiated silica material of proper size-consist may meet specification requirements.

TABLE II  
United States Silica Brick Manufacturing

	BRICKS, SHIPPED (in thousand)	TOTAL VALUE \$	VALUE (\$/thou- sand)
1952	327,997	46,797,000	142
1953	338,043	54,033,000	160
1954	226,402	37,875,000	167
1955	328,414	55,563,000	168

### Fuel Tech Meets with Industry

REPRESENTATIVES of the Solid Fuel Industry met with the staff, graduate and undergraduate students of the Department of Fuel Technology at a banquet at the Nittany Lion Inn on March 20. This annual affair is held in order to acquaint students with opportunities in the Fuel Industry, to give representatives of organizations sponsoring scholarships the opportunity to meet the recipients of such scholarships, and to review efforts to attract qualified high school students into the fuel industry.

Professor T. S. SPICER was Chairman of the Conference at which the main speaker was Joseph W. Mullen, District Engineer, Bituminous Coal Institute, whose topic was: "Why I Chose the Coal Industry." This was followed by a panel discussion moderated by Dr. G. L. Barthauer, Manager of the Technical Service Department, Research and Development, Pittsburgh Consolidation Coal Company. Other members of the panel were: Russell Flegel, District Engineer, Bituminous Coal Institute; Jack MacLachlan, Fuel Engineer, Pittsburgh Consolidation Coal Company; Charles Russell, Manager, Coal Carbonization Bureau, Research Dept., Koppers Co.; W. F. Saalbach, Personnel Advisor, Research & Development, Pittsburgh Consol; C. H. Sawyer, Assistant Sales Manager, Eastern Gas and Fuel Associates.



Silica Brick Roof Failure in an Electric Arc Furnace

The basic approaches to providing Pennsylvania silica-brick manufacturers with a proper raw material for super-duty silica brick include: (1) beneficiating all of the run-of-mine material to meet super-grade specifications, or (2) beneficiating some run-of-mine materials to make a super-grade and then blending such amounts of super-grade as are needed with run-of-mine material to make lower-grade bricks.

The relative importance of this problem for the Pennsylvania silica brick industry and the Pennsylvania economy demands continued efforts to solve this economic-technological problem. Preliminary investigations indicate this problem can be solved. It will not be easy and will require a well-planned, thoroughly detailed research program on the mineral preparation problems involved.

### REFERENCES

1. *Modern Refractory Practice*, Harbison-Walker Refractories Company, 1950.
2. *Basic Open Hearth Steelmaking*, American Institute of Mining and Metallurgical Engineers, 1951.
3. *Industrial Rocks and Minerals*, American Institute of Mining and Metallurgical Engineers.

### Ceramics Dept. Receives Grant

A GRANT of \$17,040.00 has been received from the Carborundum Company to study the influence of stresses between crystals in a ceramic refractory when it is cooled after firing where the crystals have different expansion coefficients along the areas of contact.

The research will be carried out by M. K. Murthy of Bangalore, India, under the direction of Professor Hummel, professor of ceramic technology. Dr. Murthy attended the University of Mysore and Alfred University. He received his Ph.D. in ceramic technology from Penn State in 1954, and has now returned as a research associate after spending several years in the ceramic industry in India.

The objective of the research is to examine the nature of the microstresses which arise by measuring the strength and elasticity of ceramic products at low and high temperatures. The correlation of the effects of anisotropy of expansion, microtexture, and porosity should permit the development of refractories with improved resistance to drastic temperature change.

R. L. SLOBOD, head, Department of Petroleum and Natural Gas, has been appointed for a second year as Pennsylvania's representative on the Research Committee of the Interstate Oil Compact Commission.

## MINERAL INDUSTRIES STAFF ACTIVE IN MANY FIELDS

RICHARD P. NICKELSEN, assistant professor of geology, and GERARDO GROSS, graduate student in geophysics and geochemistry, presented a paper entitled "Petrofabric Study of Conestoga Limestone from Hanover, Pennsylvania" before the 34th Annual Meeting of The Pennsylvania Academy of Science, April 4 at Lafayette College, Easton, Pa.

H. B. PALMER, associate professor of fuel technology, presented a review of work currently in progress on gaseous combustion and high-temperature gaseous reactions before the annual meeting of Project Squid held at The Bureau of Mines in Pittsburgh.

Several members of the Department of Meteorology attended the 165th National Meeting of the American Meteorological Society at Washington, D.C., which was held jointly with the American Geophysical Union, May 5 to 8. A. K. BLACKADAR, associate professor of meteorology, presented a paper on frictionally induced momentum oscillations and vertical motions in the atmosphere over the United States. PAUL R. JULIAN, instructor in meteorology, spoke on the forecasting of stratospheric winds for aircraft navigation purposes. EDWARD S. EPSTEIN, research assistant in meteorology, presented a paper entitled "The Three Dimensional Field of Motion in the Lower Atmosphere." H. A. PANOFSKY, professor of meteorology, discussed the relation between Lagrangian and Eulerian Correlation Functions, and C. L. HOSLER, associate professor of meteorology, considered the role of dilute solutions in cloud droplets in determining their freezing temperature.

E. WILLARD MILLER, head of the Department of Geography, has been appointed geographic editor for Funk and Wagnall's Universal Standard Encyclopedia.

GEORGE F. DEASY, professor of geography, and PHYLLIS R. GRIESS, associate professor of geography, presented two joint papers at the Pennsylvania Academy of Science meetings in Easton, Pennsylvania on April 4. The titles of the papers were: "Past, Present, and Future Foci of Bituminous Coal Strip Mining in Pennsylvania" and "Some Geographic Aspects of Pennsylvania's Bituminous Coal Strip Pits."

S. C. SUN, professor of mineral preparation, and W. L. McMORRIS, III, preparation engineer of the U. S. Steel Corporation, presented a paper entitled "Factors Affecting the Cleaning of Fine Coals by Convertol Process" before the annual meeting of the American Institute of Mining and Metallurgical Engineers at New York City on February 16.

J. C. GRIFFITHS, head of the Department of Mineralogy, as a member of a six-man panel, spoke on April 5 at the Annual Meeting of the American Geology Teachers Association on "The Place of Petrology in the Undergraduate Geology Curriculum;" on April 7th, Dr. Griffiths addressed the faculty and graduate students in Geology at Harvard College on "Some Problems in Sampling Sedimentary Rocks."

ROBERT N. CLAYTON, assistant professor of geo-chemistry, received a grant of \$4000.00 from the National Science Foundation for "Extraction of Oxygen for Isotopic Analysis."

## CHEMICAL BENEFICIATION GROWS IN IMPORTANCE

(Continued from page 1)

Major chemical beneficiation methods of interest to the mineral preparation engineer are the following: flotation, leaching, flocculation, cyanidation, and amalgamation. Of these flotation and leaching are the most important. The application of these processes to a given ore dressing problem depends mostly on how the valued mineral occurs. Flotation can be used successfully for the beneficiation of ores that liberate in the range of from 28 mesh (590 microns) to about 25 microns. Leaching and the other methods are generally used on extremely finely liberated ores and on ores in which the wanted elements are chemically locked or combined with other less valuable ones.

When processed in a preparation plant prior to utilization, an ore is subjected to three general types of treatment: (1) size reduction to free the mineral particles, (2) concentration to separate the mineral particles or specific elements from each other, and (3) solid-fluid treatment to recover the concentrate, or final product. In all ore deposits the useful minerals are tied up with the useless in the form of chemically or physically locked particles, and before concentration or beneficiation can take place it is necessary to liberate the useful minerals. This is accomplished by crushing and grinding operations, and these are followed by screening and classifying. These steps are necessary to condition or prepare the ore for concentration. Following the separation, the solid concentrates must be removed from the fluid. This is performed by such operations as thickening, centrifuging, filtering, and drying.

### FLotation <sup>1,2</sup>

Of the different chemical methods of beneficiation utilizing surface chemistry, froth flotation is the one most generally used today. In this process air is bubbled through a pulp (finely ground ore) suspension containing the liberated minerals. The air bubbles can be formed by mechanical agitation or by actually pumping the air into the pulp. Mechanically agitated pulps produced by sub-aeration methods have found the greatest usage in industry. Many types of flotation machines utilizing this principle are in use today.

The actual flotation of minerals is due to the differences in the chemical nature of the mineral surfaces. Some of the minerals will attach themselves to the air bubbles and be levitated to the surface where they are mechanically removed as a froth. Other minerals, usually the worthless ones, will remain in the pulp. The phenomena causing bubble attachment to minerals are promoted by use of reagents known as collectors. These collectors, of which there are many, coat all or a portion of the surface of the mineral to be removed in the froth with a greasy, water-repellent organic film, while the other minerals usually remain unaffected. As the air is introduced into the conditioned pulp the collector-coated minerals reject contact with the water phase in a manner similar to wax paper; i. e., they tend to reject the water phase and accept the air phase. Thus it may be seen that the fundamental principle involved in flotation is a "fight" between air and water for the surface of the mineral. If the

mineral is preferentially wet by air it appears in the froth, but if it is preferentially wet by water it will remain in the pulp.

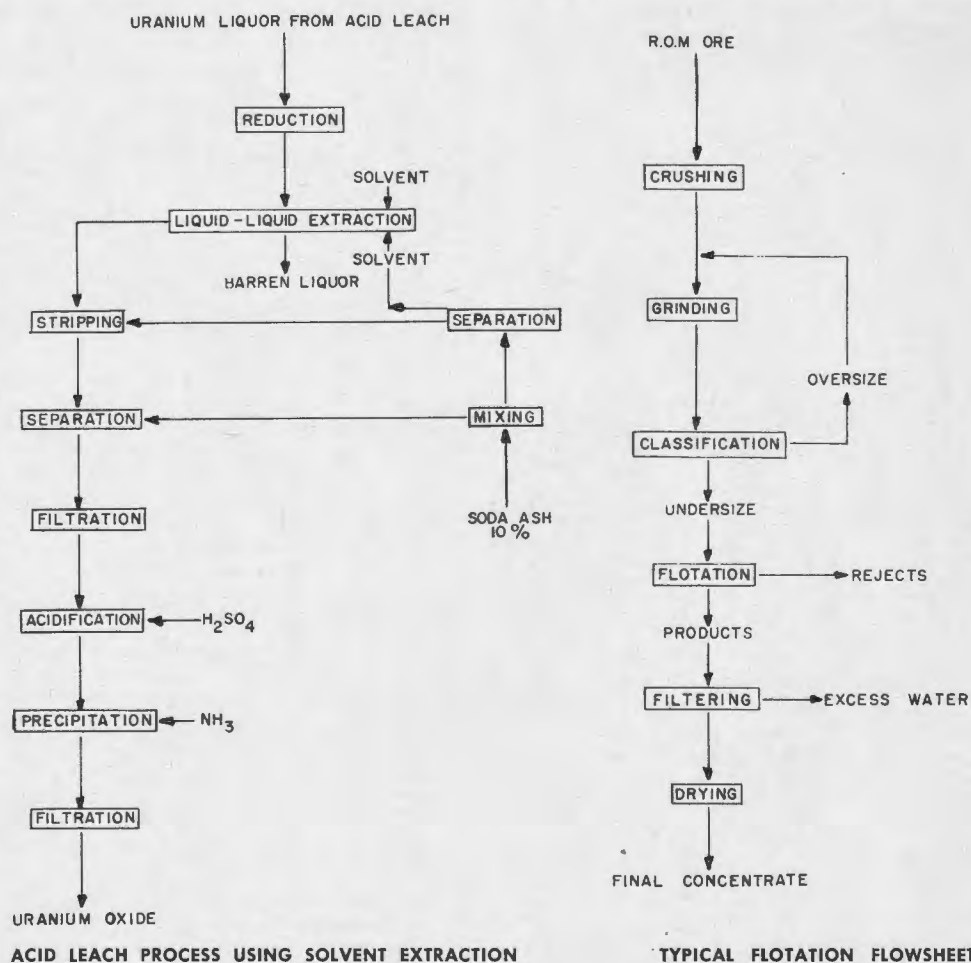
In general, collectors are aliphatic organic salts, acids, and bases which behave as simple electrolytes at the low concentrations used. Only three aliphatic homologous series are used to any commercial extent at the present time. These are xanthates, the fatty acids, and the primary amines. The aliphatic group of xanthates generally contains only two to five carbon atoms, while the aliphatic group of the fatty acids and amines generally contains from eight to twenty carbon atoms. The cations of the xanthates and fatty acids are  $H^+$ ,  $Na^+$ , and  $K^+$ , and the anions of the amines are the chlorides and acetates.

A phenomenon does not always have to be understood to be useful, and this is the situation concerning collector attachment to the mineral particle surface. The exact mechanism by which these collectors attach themselves at the surface of a mineral is not known. Whether it is some type of physical adsorption or some type of chemical reaction is a debatable problem that has occupied much time and effort. However, within recent years much progress has been made through the use of radioactive tracers. One of the greatest advances gained from this work has been the discovery that it is necessary to cover only a small fraction of the mineral surface with a monomolecular coating of the collector to render the mineral water repellent and thereby promote flotation.

A great deal of flotation research has been conducted and has resulted in the compilation of considerable data, but most of the data are true only for a specific mineral under specific conditions. There are only a limited number of basic rules applicable to the whole of flotation, and these rules are mostly the result of deductions made after exhaustive fact-finding research. The absence of a great number of common rules is understandable in view of the very large number of variables involved in the flotation process.

Generally, anionic collectors are used for minerals that are predominantly basic, and cationic collectors are used for minerals that are acidic. This generalization gives rise to the use of anionic collectors such as oleates for oxides and the xanthates for the sulfides of metals. Cationic collectors such as the amines are used widely for the collection of acidic minerals such as quartz.

Any change in the composition of an organic ion, which is already a collector, that causes a decrease in its solubility in water will increase its effectiveness as a collector. Collectors such as the oleates and xanthates become less soluble as their chain length increases, thereby becoming more effective collectors. The concentration of a long-chain xanthate therefore can be much less than that of a xanthate with a short chain to accomplish the same results. Often salts are added to the flotation process where short-chain collectors are used. This has the effect of decreasing the solubility of the collector which results in reduced reagent consumption.



tion. The water repellency of a collector can often be increased if it is accompanied by a hydrocarbon such as fuel oil or kerosene. This has the effect of coating the collector, further increasing the water repellency of the collector-coated mineral, and resulting in better recoveries.

One of the critical factors affecting the use of a collector is the pH value of the flotation pulp. Determining the optimum pH value of collection is always an important part of the work of the mineral preparation engineer. The objective is to find the pH value at which the reagent is ionized to the fullest extent. At this value more collector groups are available for attachment to the mineral surface. Common regulators used to change the pH value of the flotation pulp are sulfuric acid and sodium hydroxide.

Other reagents used in flotation are activators and depressants. Both of these groups work on selected minerals to induce collection in the case of the activator or discourage collection in the case of the depressant. Since most minerals adsorb hydrogen and hydroxyl ions over some part of the pH range, it follows that hydrogen or hydroxyl ions often act as depressants or activators. Activators can also be inorganic compounds and are chosen so that the active ion has a charge opposite to that of the collector ion. Close control is essential as excessive amounts of an activator may tend to reduce reagent effectiveness by precipitating the collector. Quite often activators contain an ion in common with the mineral to be activated.

Depressants cause selected minerals to become water wet and, therefore, to remain in the pulp during the flotation process. Depressants are compounds in which the active ion

or the ion that reacts with the mineral surface has a charge similar to the collector ion.

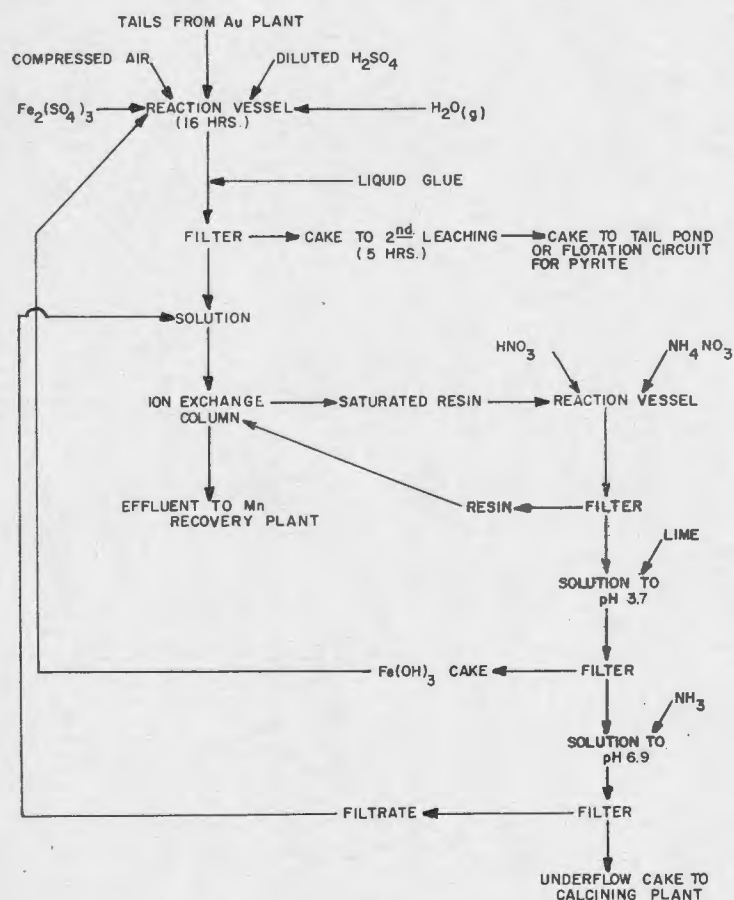
Other reagents, known as frothing agents which act at the liquid-air interface, are added to the flotation pulp to aid in the formation of froth. These are very often alcohols, acids, or amines. Perhaps the most common frother in use today is pine oil, a common household item which has found wide spread use in the ore dressing industry. In the study of froth or bubble production it has been found that an increase in frothing agent increases both the volume and stability of the froth until a critical concentration is reached, past which further reagent additions result in a decrease in froth volume and stability. Other findings indicate that a three-phase froth system is more stable than a two-phase system; i.e., an aerated pulp containing both solid and liquid phase is more stable than an aerated liquid.

In flotation practice, as in all mineral dressing, it is always desirable to grind the ore in a manner that will give the greatest number of particles at the size at which liberation occurs. The overgrinding of minerals and the resulting overproduction of fines is not economically sound. Overgrinding represents a waste of power as well as a reduction in flotation efficiency. It becomes obvious that for a given weight and size of material any decrease in size will result in an increase in the surface area. This increase in surface area causes a two-fold problem in the flotation process: (1) more collector is required to coat the greatly increased particle surface area, and (2) the increase in surface area results in an increase in surface chemical activity. This condition causes an overabun-

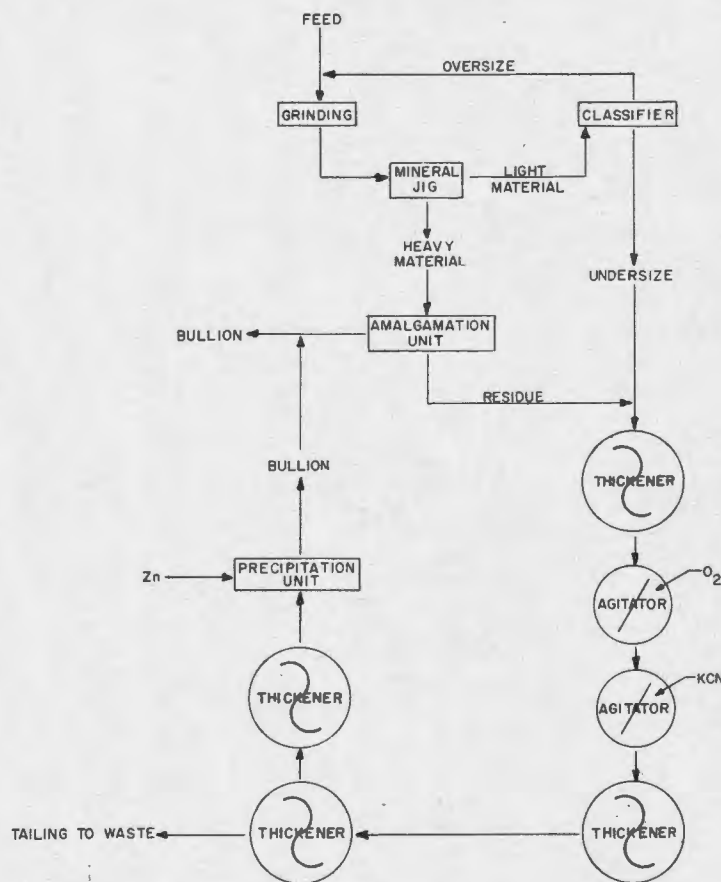
dance of ions to be present in the solution, often imparting similar surface characteristics to the minerals to be separated. This is undesirable since collection is likely to become highly unselective. This problem can sometimes be reduced by use of very dilute pulps (1 to 2% pulp density) which tends to promote natural dispersion. The lower industrial size limit of flotation is at about 25 microns, although laboratory flotation can be achieved down to about 5 microns. In any single flotation test generally the fines are first to float followed by the middle and large size particles.

Metallic ores being concentrated by flotation include copper, lead, zinc, tin, nickel, gold, silver, molybdenum, and tungsten, and recently two plants have been built for the flotation of iron ore. Nonmetallic minerals being concentrated by flotation include sulfur, potash, cement, clay, fluorspar, feldspar, bauxite, graphite, cryolite, mica, glass sand, talc, and barite. In a great many of these non-metallic processes, impurities are removed from the final products by flotation. For example iron is removed from sulfur, graphite and silica are removed from cement, and color impurities are removed from clay. One of the most interesting flotation processes for non-metallics is that of cryolite. This mineral is shipped from Greenland to Philadelphia and transported to Pittsburgh for processing. The ore deposit is the only one in the free world, and the ore originally contained 99% plus cryolite. Today cryolite shipments contain as little as 70%, and flotation to remove the impurities is necessary to raise the grade to over 98% which is required by industry.

The flotation process is also used in coal  
(Continued on page 6)



ACID LEACH PROCESS USING ION EXCHANGE COLUMN



AMALGAMATION AND CYANIDATION FLOWSHEET

## Chemical Beneficiation

(Continued from page 5)

cleaning. At present there are about 15 coal flotation plants in operation in this country. The extent to which flotation is used to clean coal, however, is quite small; less than 1% of the total coal being prepared is cleaned by flotation.

### LEACHING<sup>3,4,5</sup>

Leaching operations are probably as old as the first wet chemical procedures. Leaching reagents can be acids, bases, or salts. These reagents are pulped with the finely ground ore, after which the insoluble material is removed from the solution and discarded by thickeners or cyclones. The pregnant solution, or leach solution containing the ionized constituents, is then subjected to one of three procedures: (1) direct chemical precipitation using standard reagents, (2) removal of the desired ions by solvent extraction methods, or (3) removal of the desired ions by ion exchange resins.

The use of direct chemical precipitation methods is rapidly becoming obsolete. The principal failing in this method is that the precipitating reagents are usually unselective, and the resulting precipitate must undergo costly and often complicated purification steps. In this type of leaching large cylindrical precipitating thickeners are used in which the pregnant solution is mixed with a suitable reagent. The resulting precipitate is moved by mechanical rakes to the center of the thickener, from which it is discharged by diaphragm pumps. The solid-fluid separation is then achieved in a filter press. At present this type of leaching is being used to beneficiate copper ores. The leach solutions are either sulfuric acid or acid mine water.

Solvent extraction methods involve the use of certain organic liquids into which the pregnant solution is introduced. By thoroughly mixing the pregnant solution with the solvent, the desired valuable ions report with the organic phase. These organic liquids are generally soluble in carriers such as kerosene and, after mixing with the aqueous solution, form on top of the barren leach solution. Next, a liquid-liquid separation is made in which the immiscible organic phase is decanted from the barren solution. The immiscible organic liquid containing the valuable constituent is then stripped, or freed, from the valuable constituents by one of the following methods: (1) evaporation, (2) change of pH, or (3) chemical solutions. The method in use industrially involves chemical solutions in which the loaded organic liquid comes in contact with an aqueous solution that removes the desired component from the organic phase. This step serves a dual purpose. It yields an aqueous solution containing the valued constituents and rejuvenates the solvent for re-use. The whole process of solvent extraction is one of transferring valued constituents from a pregnant leach solution to a solvent, separating the solvent from the leach solution by mechanical methods, and finally transferring the valuable materials from the solvent to a stripping solution.

Today, solvent extraction processes provide about 8% of the uranium produced in this country. Plants are in operation successfully separating hafnium, zirconium, tantalum, and columbium, and recently much attention has been given to improving the recovery of nickel and cobalt from ammonia leaching of the Cuban laterites.

Industrially, solvent extraction does not appear to be as cheap as columnar ion exchange for low-grade ores because of solvent losses; however, it becomes competitive when high-grade ores are used. Other disadvantages are the fire hazard, emulsion formation, solvent poisoning, and mechanical leakage.

Ion exchange resins are the principal means of beneficiating uranium ores. This method accounts for about 61% of the uranium produced in this country. Ion exchange resins are insoluble, solid, hydrocarbon polymers that appear to have an inexhaustible service life. The life of a resin may be expected to be from 20 to 50 years, and about the only factor likely to modify this figure is physical degradation. The functioning of the ion exchange column is relatively simple. The resins are placed in a vertical cylinder or column, and the pregnant uranium-bearing leach solution in relatively large volume is passed through the resin. The resin absorbs the uranium until saturated, at which time the flow of pregnant solution is discontinued. The resins are then washed and exposed to a small volume of "eluant" solution. This frees the uranium from the resins, after which the resins are prepared for another cycle of operation. For continuous operation, a number of columns are used—some on stream and some under rejuvenation. Perhaps the only disadvantages of ion exchange columns are the lack of continuity and the requirement that clear liquors be used, necessitating high investments in filters and clarifying equipment.

Leaching processes are also conducted using gases in moving bed reactors. Chlorine gas passed through a bed of dry finely ground particles, resulting in the formation of volatile metal chlorides, is of considerable current interest. Chlorination techniques are now used in the well-known Kroll process for the production of titanium and zirconium. The chlorination process may be applicable also to the production of chlorides of many other reactive elements such as tungsten, molybdenum, vanadium, columbium, and silicon.

After purification, chlorides may be reduced by reaction with sodium or magnesium to produce pure metals free from oxygen or nitrogen.

With the exception of iron chloride, leach chlorides are usually distilled from the ore rather than being leached with water. This is necessary because chlorides of the more reactive metals are hydrolyzed in the presence of water to form insoluble oxides.

### FLOCCULATION<sup>6</sup>

Another chemical beneficiation process dependent upon surface chemical reactions is flocculation. In this process a chemical reagent is added to a pulp containing very finely ground particles, and the reagent makes it possible for the particles to get together to form a floc. This is very beneficial in the removal or the separation of particles from suspension in water and makes it possible to thicken the pulp before filtration. In certain cases when different minerals are present in the same pulp, it is possible to add a particular reagent which will selectively floc a given mineral and thus cause it to drop or to be removed from the suspension, thereby separating it from the other minerals.

Flocculation is generally accomplished by the addition of an electrolyte. In dealing with negatively charged particles, the cation or positive portion of the electrolyte is the more important, and, conversely, in dealing with

positively charged particles, the anion is the more important.

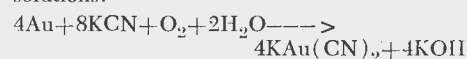
It has been known for a great many years that trivalent cations are more effective flocculating agents than divalents which in turn are more effective than monovalents. Recently, however, complex polyelectrolytes made by the polymerization of organic products have been investigated for this purpose, proved to be technically sound, and in some cases economically feasible.

One of the major flocculating problems in this country is in the Florida phosphate mining area. After removal of the overburden sand by dragline, the phosphate rock is mined by high-pressure hydraulic sluicing, and the resulting pulp is pumped into the preparation plant for processing. About one third of this material is smaller than 200 mesh or 74 microns, and in this fine stage it cannot be processed, filtered, or flocculated. To dispose of this material, it is pumped to a settling pond, but even then much of the material refuses to settle out of suspension. Many different flocculating agents have been used, but to date none have been found that could be considered entirely satisfactory.

### MISCELLANEOUS CHEMICAL PROCESSES<sup>7,8</sup>

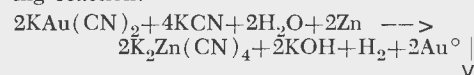
Two processes worth mentioning involve the beneficiation of gold ores and have been in use for many years—cyanidation and amalgamation. Gold does not tarnish at ordinary temperatures, nor is it soluble in sulfuric, nitric, or hydrochloric acids. It does dissolve in aqua regia, in some chlorine and bromine compounds, and in mercury with which it unites to form an amalgam. However, the main chemical property of commercial interest is the solubility of gold in dilute cyanide solutions. The basis of the cyanide process is that weak solutions of sodium or potassium cyanide have a preferential dissolving action on small particles of metallic gold and silver over other minerals usually found in gold ores.

Elmiers' equation is generally accepted as expressing the action of gold in dilute cyanide solutions:



Thus, when fresh surfaces of gold are exposed to the action of cyanide in an aqueous solution containing free oxygen, a gold cyanide compound will be formed together with a hydroxide. Temperature of the reaction is an important factor, and frequently solutions are heated to about 70°F. Below this temperature incomplete recovery may result, while at much higher temperatures loss of cyanide by decomposition becomes a serious factor.

After the solution has been clarified immediately preceding precipitation, it is necessary to remove the dissolved oxygen from the solution by a deaeration process. The gold is then removed from the solution by precipitation with zinc dust according to the following reaction:



Amalgamation is a process for separating liberated metallic gold or silver from an ore by use of mercury. In this method the ore is ground to liberation and pulped in water. The pulp is then permitted to flow across a film of mercury which is anchored to a metallic surface. The separation is made when the gold or silver is wetted by the mercury

(Continued on page 8)



# Mineral Economics

## BORAX — The Triple Use Mineral

John J. Schanz, Jr.\*

Many mineral raw materials display great versatility in their usefulness. Some serve a dual role by being employed both as metallic ores and nonmetallic minerals. Borax, however, is one of the few minerals which is utilized by all three classes of mineral industries—metal, nonmetallic, and fuel.

Borax is only one of the seven commercial boron-containing minerals. However, it is the most common boron compound in actual use, and the other six borate minerals are frequently converted to the borax form. In addition to borax, the other principal boron minerals are: kernite, colemanite, ulexite, priceite, boracite, and sassolite. There are approximately fifty additional minerals containing boron, but none of these has ever been an important commercial source.

### U. S. DOMINATES WORLD BORAX

The United States continues to dominate the world production and consumption of borax. In 1956, the United States produced 944,950 tons of boron minerals containing 315,047 tons of  $B_2O_3$  worth approximately forty million dollars. Though world production data are not available, it is reasonable to estimate that this country produces over ninety per cent of the world total. Consequently, the United States imports only insignificant quantities of borax but exports approximately twenty per cent of its production to all nations of the world.

The price of borax declined steadily from 1861 until the late 1930's. Currently, the average value of borax at the mine is approximately \$42.00 per ton, which represents a gradual increase in recent years. At this price level, borax cannot be considered a low-price nonmetallic and is not restricted to local markets. In fact, borax is a high-price specialty mineral which can be shipped great distances. The delivered prices in New York normally are about double the producer's price in California.

Three companies currently produce all of the United States boron minerals—U. S. Borax and Chemical Corporation, American Potash and Chemical Corporation, and the West End Chemical Division of Stauffer Chemical Company. United States Borax is the largest company of the three and possessed an estimated 70 per cent of the world's productive capacity prior to its present expansion program. The company mines kernite and borax near Boron, colemanite at Death Valley Junction, and ulexite near Shoshone, California. The underground mines at Boron have been converted recently to the first open-pit borax mining. Stauffer Chemical and American Potash are both processing Seales Lake brine. An additional company, California Borate Company, is in development stages, but commercial production from their property has not yet been reported.

The use of boron in the mineral, or

chemically combined form, extends back many centuries. Its well-known fluxing properties probably were utilized at an early date in the manufacture of jewelry. Other characteristics which have made borax one of our most useful minerals are its easy fusibility and solubility, its antiseptic and detergent qualities, and its effect on the properties of glasses of which it is a constituent.

### INDUSTRIAL USES OF BORAX

Its antiseptic qualities have made it a household commodity known to almost everyone. Borax and boric acid are used in disinfectants, mouth washes, tooth powders, cosmetics, lotions, and ointments. It has a wide variety of other uses in consumer goods ranging from the manufacture of candles and stove polish to tobacco.

The glass and ceramic industries have found boron compounds most useful, and they now consume about half of the United States total production. Borax is utilized primarily by the ceramic industry in making enamels and glazes. In glass, borax has two major and many minor uses. In lime-soda glasses, used for containers, tableware, etc.,  $B_2O_3$  is added to improve melting and firing conditions and to increase clarity, brilliance, strength, and resistance to thermal shock. Borosilicate heat-resistant glasses, such as Pyrex, have a low coefficient of expansion and are highly resistant to thermal and mechanical shock and to chemical action. Other uses in the glass industry are for making optical glass, electrical insulators, building blocks, and glass wool.

Agriculture, as well as virtually every American industry, also finds borax a useful material. Borax has become recognized as an essential ingredient of fertilizers used for prevention and treatment of boron-deficiency plant diseases. It is also used in insecticides, as a weed killer, in a disinfecting wash for citrus fruits, in retarding the growth of fungi in lumber, and in the cleaning, dyeing, and preserving of hides or leather.

In the late 1930's and through the World War II years, a new role in the metal industries was established for versatile borax. It became known that minute quantities of boron in steel would increase steel's hardenability, its ultimate strength, and its elastic limit. The addition of .002 per cent boron will produce hardenability in steel that is equivalent to or better than that produced by using 0.30 per cent manganese, .35 per cent molybdenum, .50 per cent chromium, or 2.00 per cent nickel. The value in times of national emergency of reducing the use of these other alloying materials, some of which are in short supply, is obvious. However, boron does not completely replace these other elements since they produce other desirable qualities in steel not furnished by boron. For example, boron reduces the amount of manganese required for hardening steel but does not yield the same deoxidizing and desulfurizing effects

as does manganese. There is a limit, moreover, to the amount of boron which can be advantageously used in making steel. When enough ferroboration is added to raise the boron content of steel above .003 per cent, there is no additional improvement in the hardenability, and hot shortness becomes a problem.

Another modern use for metals containing boron, or for elemental boron itself, has been found in atomic energy. Boron has a very large capacity for absorbing neutrons, and this characteristic can be employed in control rods and shielding for nuclear reactors. Though the initial raw material, borax, is not too expensive, pure boron is difficult to produce and 98 per cent pure boron costs about \$250 a pound.

### BORAX ENTERS FUELS PICTURE

The latest chapter in the story of borax utilization is found in its entrance into the high-energy, or "exotic", fuels picture. The old fuel standby, carbon, doesn't pack as strong a punch as some of the other elements. Carbon, with a heating value of about 13,000 Btu per pound, or 18,500 Btu per pound when combined with hydrogen in aviation gasoline, cannot match the heat value of hydrogen alone, beryllium, or boron. Of these elements boron has come in for the most attention, even though its 26,000 Btu per pound is lower than for the other two, because it is not as difficult to handle as hydrogen and is more readily available than beryllium.

Simple arithmetic indicates that an airplane utilizing a boron-based fuel with 25,000 Btu per pound compared to conventional gasoline at 18,000 Btu per pound should be able to fly approximately 40 per cent faster or farther. To take advantage of this improvement in performance the Government in 1952 sponsored an extensive research program in organometallic chemistry to develop new "chemical fuels. By mid-1957, sufficient progress had been made to make it possible for the Olin Mathieson Chemical Corporation and Callery Chemical Company to start construction of two prototype production plants for completion by 1959.

Though some automobile gasolines are advertised as "boron gasolines", they are not the chemical fuels which have been developed for military aircraft for the amount of boron added is small. The true boron fuels will be many times more expensive than normal hydrocarbons and will probably be first utilized in turbojet or ramjet aircraft. It is estimated that the first chemical bomber may need 24 tons of chemical fuel per hour. At this rate of consumption, the first two plants will only be able to keep one bomber flying for a normal number of hours during a three-month period. Because of the cost and limited supply, these first chemical bombers will probably use chemical fuels for only part of their flight to gain extra speed or additional range.

Starting with borax, the process of making boron fuels is quite complex. Diborane, an intermediate, is first produced and then subjected to heat to form pentaborane-9 and decaborane-14. In the final step these boranes are made to react with a hydrocarbon to produce the final chemical fuel. In addition to the immediate prospect for aircraft fuels, further use of the boron hydrides to make solid and liquid fuels for rocket propulsion seems probable.

Thus borax, which has proved a valuable mineral resource in so many ways for centuries, appears assured of a new era of growth

(Continued on page 8)

\*Associate Professor of Mineral Economics

## DEGREES AWARDED, COLLEGE OF MINERAL INDUSTRIES

DEPARTMENT	BACHELOR OF SCIENCE DEGREES		ADVANCED DEGREES			
	Degrees Granted June, August 1957; and January 1958	Total Number Degrees Granted Since 1894	M.S. Degrees June, August 1957 and January 1958	Total M.S. Degrees Since 1913	Ph.D. Degrees June, August 1957 and January 1958	Total Ph.D. Degrees Since 1934
Ceramic Technology	4	250	0	73	0	37
Fuel Technology	1	114	1	29	1	31
Geography	10	75	8	28	2	6
Geology and	} 15	} 213	2	45	1	4
Mineralogy			5	27	1	16
Geophysics and	} 4	} 37	1	15	2	5
Geochemistry			0	7	4	5
Metallurgy	22	781	1	81	1	19
Meteorology	41	256	6	43	1	7
Mineral Economics	4	54	5	20	0	1
Mineral Preparation	2	30	2	17	0	2
Mining	10	595	2	49	0	4
Petroleum and Natural Gas	19	332	5	74	2	16
COLLEGE TOTAL	132	2737	38	508	15	153

## Professor Reagan Retires from Metallurgy Department

W. J. REAGAN, associate professor of metallurgy, retired from his post at the University January 31, after having been on the faculty since July 1, 1946.

During his association with the University and while employed in industry, Professor Reagan was the author of many articles and papers concerning the iron and steel industry. He has also been a consultant for many companies in the field of metals and is continuing this work on a larger scale following his retirement.

He has been active in and is a member of the American Institute of Mining, Metallurgical and Petroleum Engineers, The American Society for Metals, The Association of Iron and Steel Engineers, The Pennsylvania Society of Professional Engineers and the Engineers Society of Western Pennsylvania.

Professor Reagan is a charter member and past chairman of the National Electric Furnace Conference and a recipient of its Statuette Award. He is a 25-year member of the American Society for Metals.

## Chemical Beneficiation

(Continued from page 6)

and engulfed into the mercury phase. For amalgamation to be effective it is necessary that: (1) the gold and silver are only metallic substances in the ore, (2) they are relatively soluble in mercury and insoluble in water, and (3) the surface tension of mercury is high enough to permit it to engulf the gold and silver. The process of amalgamation, because of these restricting conditions is not in common usage.

## REFERENCES

1. K. L. Sutherland and I. J. Wark, *Principles of Flotation*, Brown, Prior, Anderson Pty. Ltd., Melbourne, Australia, 1955, First edition, 489 p.
2. A. F. Taggart, *Elements of Ore Dressing*, John Wiley and Sons, Inc., New York, N.Y., 1951, First edition, 595 p.
3. G. H. Morrison and Henry Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley and Son, Inc., New York, N.Y., 1957, First edition, 269 p.
4. L. W. Coffey, "Atomic Age Metal Extraction," *Chemical Engineering*, Vol. 65, No. 2, January 27, 1958, 107-122 p.
5. R. E. Vener, "Moving-Bed-Process-Present and Potential Applications," *Engineering and Mining Journal Handbook of Ideas for Better Mine, Mill and Smelter Operations*, 1957, 95-105 p.
6. H. B. Charnbury, "The Chemical Beneficiation of Minerals," paper presented before the Southeastern Section of the American Chemical Society at Gettysburg College, Gettysburg, Pennsylvania, May 26, 1955. Not published.
7. Anonymous, "Cyanidation of Gold Ores," *Publications of the Denver Equipment Company*, Denver, Colorado, Bulletin No. M3-B7.
8. A. F. Taggart, *Handbook of Mineral Dressing*, John Wiley and Son, Inc., New York, N.Y., September 1950, Fourth edition.

Mineral Industries  
May 1958

## Borax — The Triple Use Mineral

(Continued from page 7)

and usefulness. This has been reflected in the considerable investor interest in companies producing borates or chemical fuels. Exploration for borates has also picked up. Although borate reserves in the United States have been considered adequate for many years to come at the present rate of depletion, the possibility of more rapid depletion of these reserves could cause considerable shortening of their life expectancy.

THE ATOMIC ENERGY COMMISSION has renewed for the fifth time its support of research on the "Chemical Nature of the Organic Matter of Uraniferous Shales." The contract amounts to \$11,880 for 1958.

Under the direction of C. R. Kinney, professor of fuel technology, at The Pennsylvania State University, a study is being made of the organic substances in uraniferous shales of interest to the Commission in an attempt to find out what the organic matter is and what it can be used for.