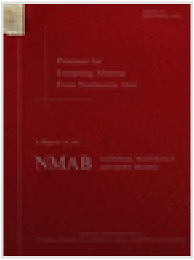

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PROCESSES FOR EXTRACTING ALUMINA FROM NONBAUXITE ORES

REPORT OF

THE PANEL ON POTENTIALS
OF ALUMINUM EXTRACTIVE PROCESSES

of the

COMMITTEE ON THE TECHNICAL ASPECTS OF
CRITICAL AND STRATEGIC MATERIALS

NATIONAL MATERIALS ADVISORY BOARD
Division of Engineering - National Research Council

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The quantitative data published in this report are intended only to illustrate the scope and substance of information considered in the study, and should not be used for any other purpose, such as in specifications or in design, unless so stated.

The findings and conclusions expressed in this report do not necessarily reflect the views of the government agencies that had liaison representation on the Panel.

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I. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

A. An acid process for the treatment of clay appears the most promising for the economic production of alumina from materials other than commercial bauxite. The available experimental and pilot plant data for producing alumina from clay appear sufficient to conclude that most of the alkaline processes normally cannot compete economically with acid processes.

Except for meeting the acceptable industry maximum of 0.03 percent Fe_2O_3, the technical feasibility of producing reduction-grade alumina by the hydrochloric extraction from clay has been demonstrated on a small scale. Probably, there would be significant economies in a production plant of large tonnage. This and other economic factors cannot be evaluated except by relatively large and extensive pilot-plant testing.

This Panel recommends that, to obtain comparative figures on the viable acid processes, the Bureau of Mines, with the financial help and cooperation of the domestic aluminum producers, (1) choose a specific HCl process for producing alumina from clay and build and operate a pilot plant of from 1 to 5 tons per day, and (2) select a nitric acid process for producing alumina from clay and build and operate a pilot plant from 1 to 5 tons per day. Hopefully, all of the producers would find it to their advantage to participate.

If the results from either of these pilot plants are successful, a larger pilot plant of 50 to 100 tons per day should be built to obtain the data necessary for scaling up to commercial plant size.

B. Another source of alumina worthy of consideration and more research is the dawsonitic [dawsonite-$NaAl(OH)_2CO_3$] deposits associated with oil shales in the Colorado-Wyoming-Utah area. The large quantity of this potential domestic source of alumina and oil is sufficient incentive to continue the current investigations by the Bureau of Mines and others for more general information and better extractive methods. However, at the present state of technology, a great part of the commercial value of the dawsonitic shales might be lost if nuclear in situ processing were conducted on them.

The Panel recommends that the Bureau of Mines expand its present research program on dawsonite. The program should include detailed mineral surveys of the extent and value of the deposits, the technical variables affecting various recovery processes, and the economics of alumina production in relation to both the sodium and the associated oil industries.

C. The production of alumina from aluminum phosphate rock does not appear economically feasible even if P_2O_5 were recovered as a by-product. Only increased return from potential additional by-products, such as uranium and cement ingredients, could change the economic outlook.

D. The production of alumina from anorthosite does not appear economically practicable using present technology because of the high processing costs.

E. The recovery of alumina from copper leach solutions may prove economic but does not represent a potentially large source of supply.

F. Today, insufficient information is available to evaluate saprolite or aluminous shale as potential domestic sources of alumina. Very large tonnages of aluminous saprolite exist and could be strip mined after removal of a thin layer of soil. Although aluminous shale is inexhaustible, no action is recommended presently on this source.

G. The quantities of ash generated at any one place are insufficient to be considered as a raw material of aluminum. Future restrictive requirements on atmospheric pollution might reduce further the amount of ash generated at localities where aluminous raw material would be desired. The use of coal ash as a source of alumina also may be lessened by the following: (1) the wide range of alumina contents of ash make raw material quality control difficult or costly and (2) much coal ash has been so vitrified that the alumina present is in a relatively insoluble form.

H. Alunite has little potential of being a major raw material of aluminum in this country because all known deposits are either small and scattered or have the mineral disseminated through volcanic rock. Alumina extracted from such material would not be competitive in price.

I. To date, none of the new reduction technologies which have been developed--including direct reduction--have been attractive economically.

J. The electrolysis of aluminum chloride, based on current attempts, is unlikely to compete successfully with the Hall process. Future technological advances in materials of construction might permit a different conclusion.

II. INTRODUCTION

The objective of the Panel on Potentials of Aluminum Extractive Processes was to assess the technological problems and potentials of utilizing resources for aluminum, other than commercial grades of bauxite, in the relatively economic production of alumina, and to indicate areas of further research.

In attempting to assess the urgency for developing alternate sources of alumina, the long-term availability of bauxite is a primary consideration. Current annual world consumption of bauxite is about 50 million tons. Current world reserves of bauxite are approximately 8 billion tons and very large potential resources of bauxite are known to exist in several countries. Projecting the annual growth of aluminum production at $7\frac{1}{2}$ percent up to 1990, the bauxite consumed in the next twenty years would amount to approximately 2.5 billion tons. Without further bauxite discoveries and assuming consumption at the rate projected for the year 1990, there are more than ample reserves of bauxite for the next twenty years. Although the cost of mining is expected to increase, the cost of alumina is not expected to rise more than a few dollars per ton. On strictly economic grounds, any potential alternate for bauxite should yield alumina close to current costs, if it is to be considered viable in the future.

In 1969, an estimated 30 percent (approximately 1,550,000 tons) of the domestic demand for aluminum was produced in this country. Of this figure, approximately one-third (500,000 tons) were produced from bauxite and two-thirds (1,050,000 tons) were obtained from secondary aluminum. Calculations based on U.S. Bureau of Mines projections indicate that for 1975 domestic production of aluminum from these sources will drop to 25 percent of the demand.

Domestic clays are a potentially immense source of alumina and warrant research into methods for their economic exploitation. To date, many processes for the extraction of alumina from clay have been investigated, but none have been economically feasible.

Another possible source of alumina worthy of more research is the dawsonite associated with some oil shales in the Colorado-Wyoming-Utah area. The tremendous tonnages of oil shale and associated dawsonite provide a great domestic resource. The dawsonite might be potentially attractive, if oil extraction were economically feasible.

III. FUTURE ALUMINUM SUPPLY-DEMAND RELATIONSHIPS

A recent assessment by the Bureau of Mines of contingent technologic, economic, and social developments, and their probable effects on the future demand for aluminum, indicates that, by 1985, the annual domestic requirements for primary (newly mined) aluminum will be between 9 and 12.7 million tons. This is equivalent to a two- to three-fold increase of the 1970 level. As indicated in Figure 1, by 1985 the increase in demand in the rest of the world is expected to be greater.[1]

Principal factors contributing to the high demand forecast include (1) the anticipated growth of electric energy consumption, (2) the increased use of aluminum in transportation and in a wide variety of consumer and capital goods, and (3) the availability and low anticipated costs of aluminum relative to competing materials such as copper, wood and plastics. Over the long term, the main contingency factors that could result in the low demand forecast are possible changes in the means of transmitting electric energy, substitutions for aluminum (especially in machinery and equipment and in the building and construction industry), and possible shifts in the processing, handling and distribution of food.

Aluminum is the third most abundant element in the earth's crust and, in this sense, the supply potential is limited only by its price. Current demand, technology, and cost limit the commercial raw material essentially to bauxite. Most of the bauxite reserves are in the less industrialized areas of the world,

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[1] Bureau of Mines Minerals Facts and Problems, Aluminum Chapter, Bulletin 650, 1970, pp. 323-343.

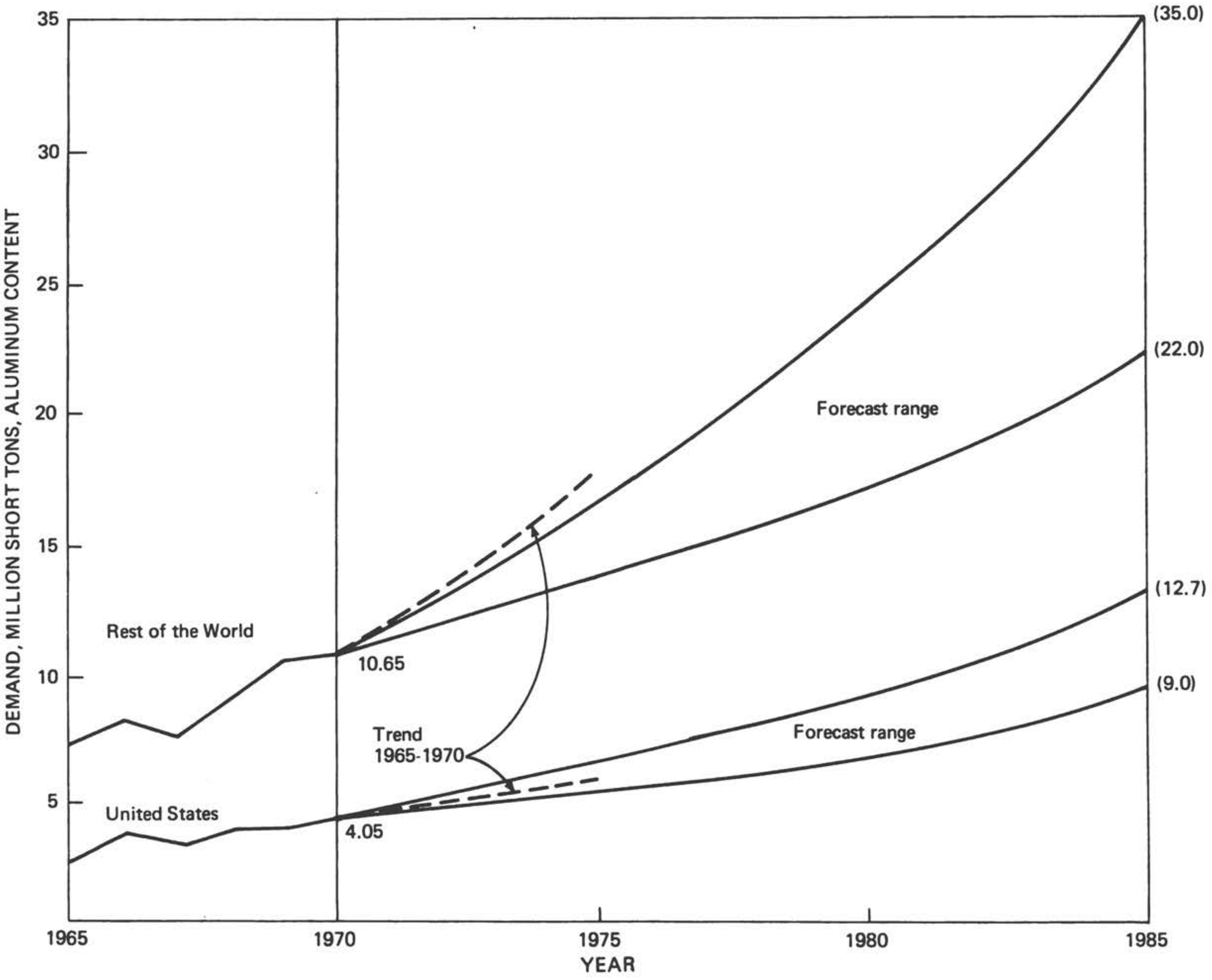


Figure 1. World Demand for Primary (Newly Mined) Aluminum, 1965 to 1970 and Projected 1970 to 1985.

far from aluminum reduction and consumption centers. Accordingly, for many years the United States and other aluminum consuming countries have considered the possibilities for making aluminum from raw materials other than bauxite.

Through 1985, the anticipated world supply of bauxite, at reasonable costs, is sufficient to meet the higher forecast of cumulative world demand. However, the United States probably cannot continue to mine domestic ore sufficient for current U. S. production of aluminum. Through research, presently known domestic resources and alternate sources of aluminum might be utilized to provide as much as 8 percent of the low cumulative aluminum demand forecast or 6 percent of the high forecast. The remainder of domestic aluminum requirements is expected to be accessible, at a cost somewhat higher than 1970, from adequate foreign sources of bauxite and alumina (or as metal).

Deposits of low-grade bauxite and non-bauxite aluminum-bearing minerals, some of which contain as much as 35 percent alumina, occur in several parts of the United States. Currently, it is not economic to extract aluminum from these materials while bauxite containing as much as 50 percent alumina is plentiful and readily available. Nevertheless, considerable research by industry and government has been directed toward developing an economic process to produce the metal from such resources.

The reasons for this are chiefly economic; however, other factors such as a desire for a dependable domestic source of raw materials, also play a part. In the iron industry, for example, economic factors have led to utilization of domestic ore, which in the 1950's was considered submarginal. In the U. S. S. R., large scale utilization of non-bauxite alumina resources probably is a compromise between economic and strategic factors.

Alternate sources of aluminum, such as clays of the kaolin type, are in great abundance throughout the world. By the turn of the century, an important percentage of new aluminum production might be derived from such materials, and could be firmly established as a basic aluminum source. Under conditions of increasing cost or stringency in foreign aluminum supplied or improvements in extraction technology, the United States could meet most of its needs for this metal from its large supplies of nonbauxitic materials. The employment, revenue, and other benefits from such a change in the pattern of source material and geographic location of supply would augment the industrial strength of the United States. Accordingly, any technological advance that promises to improve upon the present technology of winning aluminum from clay, dawsonite, or other material and to reduce significantly (about 25 percent) the economic disadvantages of presently known technology, deserves a large measure of attention.

Information in Table 1 depicts salient historical aluminum supply-demand relationships during the period 1965-1969, and their trend projections to 1975. In the period 1965-1969, the growth rate of world aluminum metal production averaged 8.6 percent per year and is projected in Table 2 from 1969 to 1975. Also in Table 2, domestic production of alumina and aluminum metal is projected at 3 and 7 percent per year, respectively, at about the same rates achieved during the 1965-1969 period. Most of the data in Table 1 are derived from these three basic projections, using the rationales indicated in Table 1.

The aluminum content of bauxite and alumina is estimated to be 25 percent and 52.9 percent, respectively, regardless of source. Statistical inaccuracies, the diverse forms and sources of aluminum materials included, the errors in estimating aluminum content, and processing losses, all result in an apparent surplus of total U.S. supply over the accountable demand, exports and stocks (see Figure 2). Accordingly, a "normal" surplus supply is calculated from the

TABLE 1. Aluminum Supply-Demand Relationships, 1965-1969 and Projected 1970-1975
(Thousand Short Tons - Aluminum Content)

	1965	1966	1967	1968	1969	PROJECTED						Rationale
						1970	1971	1972	1973	1974	1975	
World Primary Production (Mine Output):												
(1) United States	463	503	463	466	498	470	470	470	470	470	470	Assumed constant
(2) Rest of World	9,855	10,709	11,826	11,540	13,508	14,230	16,330	17,330	18,730	20,730	22,930	1/
Total	10,318	11,212	12,289	12,006	14,006	14,700	16,800	17,800	19,200	21,200	23,400	1/
Components of U.S. Supply:												
(1) U.S. Mine Production	463	503	463	466	498	470	470	470	470	470	470	Assumed constant
(2) Imports (Total)	3,946	4,225	4,354	4,611	4,996	5,496	5,918	6,485	6,818	7,377	7,931	
(3) Bauxite (including Calcined)	3,233	3,321	3,342	3,166	3,474	3,667	3,776	3,879	3,988	4,094	4,252	Total U.S. demand less production
(4) Alumina	120	259	504	697	997	1,084	1,369	1,644	1,892	2,171	2,500	Total U.S. demand less production
(5) Metal	593	645	508	748	525	745	773	962	938	1,112	1,179	Adjusted to balance supply
(6) Industry Stocks Beginning of Year (Total)	1,233	1,202	1,465	1,625	1,508	1,488	1,559	1,631	1,702	1,774	1,847	16 percent of total U.S. supply (line 17)
(7) Bauxite	833	852	1,042	1,004	1,004	1,015	1,056	1,098	1,139	1,181	1,224	Correlated with alumina production
(8) Alumina	303	285	348	402	433	433	463	493	523	553	583	Correlated with alumina production
(9) Metal	97	65	75	219	71	40	40	40	40	40	40	Adjusted to total (line 6)
(10) Secondary Aluminum Alloys Recovered, (Total)	829	887	879	940	1,004	1,116	1,204	1,315	1,366	1,455	1,542	Line 11 plus line 12
(11) From New Scrap	624	700	703	766	809	866	924	1,015	1,066	1,155	1,232	16.5 percent of total metal demand
(12) From Old Scrap	205	187	176	174	195	250	280	300	300	300	310	2/
(13) Stockpile Release (or Acquisitions) (Total)	(88)	457	74	89	169	30	50	80	100	120	130	Sum, lines 14, 15, and 16
(14) Alumina	—	—	—	—	—	—	—	—	—	—	—	Assumed zero
(15) Bauxite	(143)	149	28	31	31	—	—	—	—	—	—	Assumed zero
(16) Metal	55	308	46	58	137	30	50	80	100	120	130	Contractual obligations for total industry purchases during 1970-1975
(17) Total U.S. Supply	6,383	7,274	7,235	7,729	8,175	8,600	9,201	9,981	10,456	11,196	11,920	Sum, lines 1, 3, 4, 5, 6, 10, and 13
Distribution of U.S. Supply and U.S. Demand Pattern:												
(18) Industry Stocks, End of Year (Total)	1,202	1,465	1,625	1,508	1,488	1,559	1,631	1,702	1,774	1,847	1,919	Beginning stocks (line 16) of following year
(19) Bauxite	852	1,042	1,004	1,004	1,015	1,056	1,098	1,139	1,181	1,224	1,266	Beginning stocks (line 16) of following year
(20) Alumina	285	348	402	433	433	463	493	523	553	583	613	Beginning stocks (line 16) of following year
(21) Metal	65	75	219	71	40	40	40	40	40	40	40	Beginning stocks (line 16) of following year
(22) Exports (Total)	548	526	658	808	840	818	952	1,066	1,119	1,195	1,293	Sum, lines 23 and 24
(23) Alumina (and Bauxite)	233	196	292	457	402	500	550	600	650	700	750	Assumed 50,000 tons per year increase
(24) Metal	315	330	366	351	438	318	402	466	469	495	538	4.7 percent of total supply (line 17)
(25) Demand (Total)	4,226	4,697	4,610	5,189	5,391	5,750	6,115	6,675	7,000	7,557	8,070	Trend, 1965-1969
(26) Bauxite (Total)	255	273	261	261	271	270	275	275	280	282	285	Trend, 1965-1969
(27) Abrasive and all Other	99	103	87	83	86							Not projected
(28) Chemicals and Allied Products	73	82	86	91	95							Not projected
(29) Refractories	83	88	88	87	90							Not projected
(30) Alumina (Total) (Distribution Withheld)	182	199	202	206	220	230	240	250	260	275	285	Trend, 1965-1969
(31) Metal (Total)	3,789	4,225	4,147	4,722	4,900	5,250	5,600	6,150	6,460	7,000	7,500	Trend, 1965-1969 4/
(32) Building & Construction	961	994	967	1,138	1,220							Not projected
(33) Transportation	898	977	890	992	930							Not projected
(34) Consumer Durables	430	455	416	498	530							Not projected
(35) Electrical	541	650	624	668	710							Not projected
(36) Machinery & Equipment	289	327	309	347	350							Not projected
(37) Containers & Packaging	328	370	434	513	600							Not projected
(38) Other	342	452	507	566	560							Not projected
(39) Total U.S. Distribution	5,976	6,688	6,893	7,505	7,719	8,127	8,699	9,443	9,893	10,599	11,282	Sum, lines 18, 22, and 25
Apparent Supply-Demand Relationships:												
(17) Total U.S. Supply	6,383	7,274	7,235	7,729	8,175	8,600	9,201	9,981	10,456	11,196	11,920	Sum, lines 1, 3, 4, 5, 6, 10, and 13
(39) Total U.S. Distribution	5,976	6,688	6,893	7,505	7,719	8,127	8,699	9,443	9,893	10,599	11,282	Sum, lines 18, 22, and 25
(40) Apparent Surplus	407	586	342	224	456	473	502	538	563	597	638	Line 17 less line 39
(41) Normal Surplus 3/	355	385	403	418	456	473	502	538	563	597	638	
(42) Calculated Supply Surplus (Deficit)	52	201	(61)	(194)	0	0	0	0	0	0	0	

1/ Projections of total World Primary Production were based on the ratio of Primary Production (mine output) to Primary Metal Production (1.46 to 1) during the period 1965-1969. Rest-of-World Primary Production was obtained by subtracting U.S. Primary from World estimate.

2/ Estimates of Old Scrap supply are based on the assumption that aluminum reenters the market as old scrap, fifteen years after it first entered as new metal. Estimated quantity is related to total demand fifteen years prior to the year shown.

3/ See Table 2.

TABLE 2. **World Production of Alumina and Aluminum and Demand for Primary Aluminum (Thousand Short Tons Aluminum Content)**

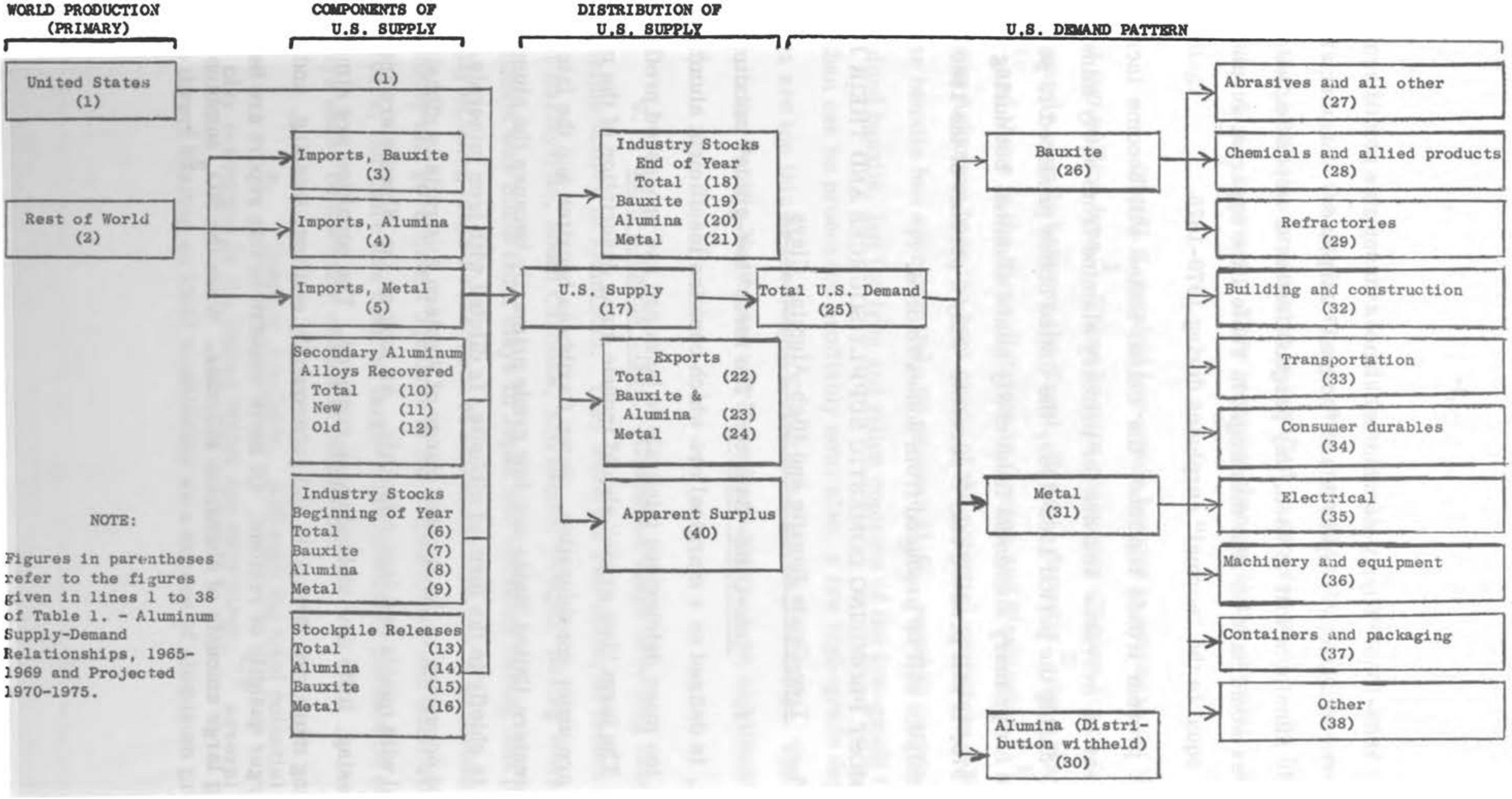
	1965	1966	1967	1968	1969	PROJECTED					
						1970	1971	1972	1973	1974	1975
Production											
Alumina											
United States	3,122	3,281	3,445	3,408	3,600	3,700	3,800	3,900	4,000	4,100	4,250
Rest of World	3,987	5,016	5,278	6,450	6,800	7,100	8,500	9,200	10,300	11,400	12,850
Total 1/	7,109	8,297	8,723	9,858	10,400	10,800	12,300	13,100	14,300	15,500	17,100
Aluminum Metal											
United States	2,754	2,968	3,269	3,255	3,793	3,840	4,150	4,450	4,725	5,025	5,425
Rest of World	4,197	4,615	5,083	5,609	6,207	6,560	7,350	7,750	8,675	9,475	10,575
Total	6,951	7,583	8,352	8,864	10,000	10,400	11,500	12,200	13,400	14,500	16,000
Demand for Primary 2/											
United States 3/	2,960	3,336	3,267	3,783	3,848	4,050	4,368	4,835	5,071	5,540	5,936
Rest of World	7,390	7,877	7,465	8,756	10,158	10,650	12,462	12,965	14,129	15,660	17,464
Total 4/	10,350	11,213	10,732	12,539	14,006	14,700	16,800	17,800	19,200	21,200	23,400

1/ Data for 1969 and projected to 1975 based on ratio world alumina production to aluminum metal production of 1.07 for 1965-1968 period.

2/ Bauxite.

3/ Total U.S. demand less supply from U.S. secondary.

4/ Projection based on ratio of primary demand to world production of aluminum metal of 1.46 for period 1965-1969.



NOTE:

Figures in parentheses refer to the figures given in lines 1 to 38 of Table 1. - Aluminum Supply-Demand Relationships, 1965-1969 and Projected 1970-1975.

Figure 2. Supply-Demand Relationship - Aluminum

data for 1965-1968. Supply-demand imbalances during this period are the deviations between apparent surpluses and "normal" surpluses. Inasmuch as only the available aluminum will be used, any prognostication of impending shortages or surpluses would have no real meaning. In Table 1 the apparent surpluses are exactly equal to the "normal" surpluses during 1970-1975.

If present trends continue, the United States will become increasingly dependent on overseas sources for primary alumina from newly mined bauxite. Indeed, during the period 1965-1969, the United States produced 13 percent of its demand for primary aluminum from newly mined alumina, but during the period 1970-1975, it will produce only 8 percent. Only 5 percent of the 1980 requirement for aluminum will be produced from domestic ores.

IV. MOST PROMISING DOMESTIC SUPPLY SOURCES AND THEIR PROCESSING

A. Low-Grade Bauxite and High-Alumina Clays

1. Low-Grade Bauxite. The term "low-grade" bauxite, as used herein, is defined as a marginal ore which contains insufficient alumina hydrates or has too many deleterious minerals to be mined and processed profitably in 1970. The term "low grade" should include some description of the mineralogy of the ore under consideration. Some Caribbean bauxites and the laterites in the Northwestern United States are low grade primarily because the alumina hydrate, which is chiefly in the form of gibbsite, is diluted with iron minerals. The bauxite occurring in the Darling Range of Western Australia is gibbsitic bauxite diluted with quartz and iron minerals. As long as the diluents are inert in Bayer processing, little new technology is required. The penalties are simply those of handling more raw materials and subsequently settling, washing, and disposing of the larger quantity of residue. Of more concern in this report are bauxites containing large amounts of aluminum silicates. When the SiO_2 combined as

aluminum silicates approaches 0.15 times the Al_2O_3 content of the ore, the cost of the Na_2O lost in the desilication product formed in the Bayer process becomes so high that additional processing is justified to recover most of the Na_2O and (or) to increase Al_2O_3 recovery. This requires changes in the chemistry and processing.

The U.S. total of low-grade bauxite is estimated at the rounded figure of 300 million tons.[1] These bauxite resources (Figure 3) are divided approximately equally between the Kauai, Hawaii, deposits,[2] the Arkansas Bauxite region,[3] and those in the three districts in Oregon and Washington.[4,5] The deposits in Arkansas have the best grade of the potential resources. Much of the Arkansas bauxite has approximately 50 percent Al_2O_3, equal to current commercially mined bauxite, but the iron and silica contents of the low-grade bauxite are higher than can be processed profitably now; also, a few high-grade deposits in this area are too thin or too deeply buried to be mined profitably. The bauxite deposits in the Pacific Northwest and Hawaii are high in iron and titanium (Table 3).

2. High-Alumina Clays. Aluminous clays have long been considered as a possible source of aluminum. They were the raw material tested in pilot plants at Harleyville, South Carolina, and Salem, Oregon, during World War II, and aluminum was made from clays in Japan and Germany during that period. The possibility of using clays as a source of aluminum also has been investigated by both industry and government agencies in the United States and other countries in recent years, but there has been no large-scale profitable production of aluminum from clays under competitive economic conditions.

a. Quantity Available. Although the total potential high-alumina clay resources in the United States are very large,[1,6] several factors having a direct bearing on their availability as a source of aluminum greatly

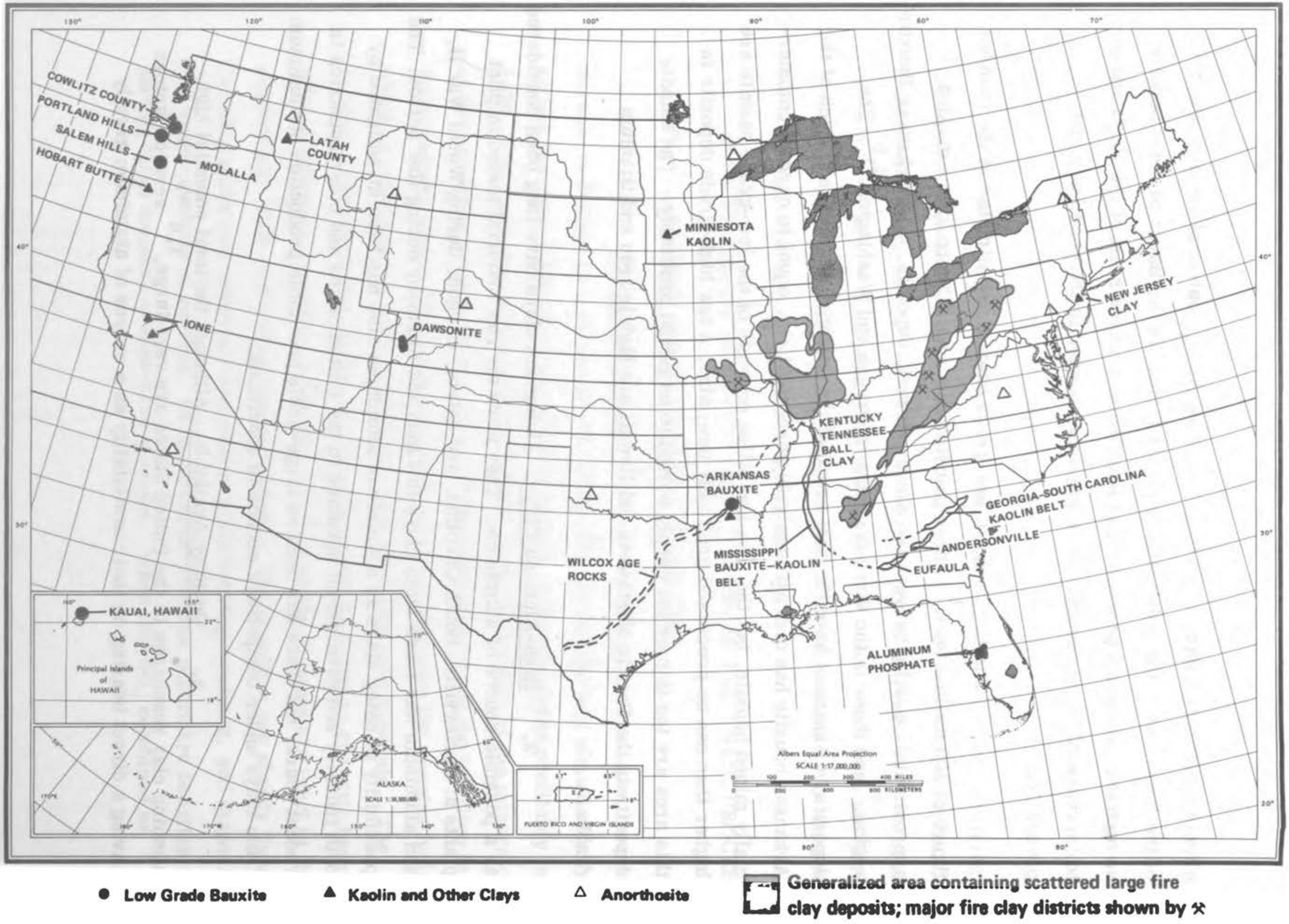


Figure 3. **Low grade bauxite and other potential sources of aluminum in the United States**

TABLE 3. Representative Analyses, in Percent, of Low-Grade Bauxite Resources in the United States

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Loss on Ignition (L. O. I.)	References
Arkansas	40 to 50	SiO_2 greater than 15.0 or Fe_2O_3 greater than 6.0, or both oxides greater than these cutoffs		1 to 3		(2)
Oregon	35.0	6.7	31.5	6.5	20.2	(3)
Washington	38.8	6.6	28.7	4.2	21.7	(4)
Kauai, Hawaii	25.9	4.7	39.4	6.7		(5)

reduce the quantity that can logically be considered an aluminum resource now. One of the main factors decreasing their availability is that many of the larger and better grade deposits, existing under geologic conditions permitting strip mining, are now owned by companies mining them for paper filler and coater, refractory products, catalysts, ceramics, and numerous other products. The value of many of these clays for several products exceeds the value that can be assigned to a nonbauxite raw material for aluminum; and, therefore, many deposits should be considered no longer available as a potential resource of aluminum. Other very large deposits of high-alumina clays occur under overburden too thick for stripping, and the added costs of underground mining would not permit their profitable use for aluminum. Some high-grade clays occur in scattered lenticular deposits; and quantities within the limits of allowable raw material transportation costs are not as much as 50 million tons, the minimum size cutoff used in this report. Still other deposits of very large size are low grade because they contain sand impurities. Several such deposits could be beneficiated by washing and high-alumina clay recovered from them but the upgrading would add to the raw material costs.

Because of the problems outlined in the foregoing paragraph and the proprietary nature of reserves under private ownership, the Panel could arrive at only the few following broad generalizations on the availability of high-alumina clay for aluminum. The most likely areas where clay containing approximately 35 percent alumina and in deposits of 50 million tons or more can be considered available for aluminum are: (1) the Georgia-South Carolina kaolin belt (Figure 3) in which deposits are of Cretaceous age; (2) a belt of Eocene Age deposits which includes the Andersonville district, Georgia, and extends northeast and southwest of this area; and (3) the Arkansas bauxite region. The total kaolin resources in Georgia which include the first two areas has been estimated mainly on geologic inferences to be as much as 3 billion tons. According to one estimate,[1] the resources of kaolin associated with the bauxite in the Arkansas region are approximately 100 million tons. Another estimate[6] lists the total amount of clay in the bauxite region and in the belt of Wilcox age rocks extending to the southwest as nearly 550 million tons. The smaller estimate is for kaolin that is 35 percent alumina, and the larger one, not only applies to a bigger area, but is for clay that has a lower average alumina content of approximately 31 percent. Information is not available on how much of the huge resource in Georgia is under overburden within the limits of profitable strip mining and how much of this clay is controlled or could be acquired at a reasonable cost by the aluminum industry. Nevertheless, the resources in these areas are of such size that they can be considered large potential sources of aluminum. The quantities available for aluminum are also likely to increase considerably as improvements are made in the efficiency of earth-moving equipment in the future and deeper deposits become profitable to mine.

In addition to the three favorable areas, outlined above, deposits of clay containing 30 percent alumina or slightly less occur in several areas, and some of these eventually may be used as a source of aluminum. Such deposits probably occur in (1) the Eufaula district, Alabama (Figure 3); (2) Kentucky-Tennessee ball-clay district; (3) at scattered localities in the belt of Wilcox age rocks between the Arkansas bauxite region and south-central Texas; and (4) in fire-clay deposits, some of which are much richer in alumina than 30 percent, at several scattered localities. They may also exist in the Mississippi bauxite-kaolin belt; in the Cowlitz County, Washington deposits; in the Molalla and Hobart Butte district, Oregon; in the Ione clays, California; and in deposits in Minnesota and New Jersey. Deposits in Latah County, Idaho, containing approximately 25 percent alumina have been considered as a source of aluminum, and deposits of this grade or somewhat lower in alumina occur at several places in the United States.[1,6]

REFERENCES

1. Patterson, S. H., Bauxite Reserves and Potential Aluminum Resources of the World: U.S. Geological Survey Bulletin 1228, 1967, 176 pp.

2. Patterson, S. H., Investigations of Ferruginous Bauxite and Plastic Clay Deposits on Kauai and a Reconnaissance of Ferruginous Bauxite Deposits on Maui, Hawaii: U.S. Geological Survey, Open File Report, 1962, 86 pp., appendix 249 pp., p. 2.

3. Gordon, Mackenzie, Jr., Tracey, J.T., Jr., and Ellis, M.W., Geology of the Arkansas Bauxite Region: U.S. Geological Survey, Prof. Paper 299, 1958, 268 pp., p. 168.

4. Corcoran, R.E., and Libbey, F.W., Ferruginous Bauxite Deposits in the Salem Hills, Marion County, Oregon: Oregon Department of Geology and Mineral Industries, Bulletin No. 46, 1956, 53 pp., p. 1.

5. Livingston, V.E., Jr., Geology and Mineral Resources of the Kelso-Cathlamet Area, Cowlitz and Wahkiakum Counties, Washington: Washington Division of Mines and Geology, Bulletin No. 54, 1966, 110 pp., p. 89.

6. U.S. Bureau of Mines (staff), Potential Sources of Aluminum: U.S. Bureau of Mines Inf. Circ. 8335, 1967, 148 pp., p. 38.

B. Acid Processes for Clays

1. General. Numerous investigations indicate that an acid extraction process is preferred over alkaline ones for treating clays. A series of Bureau of Mines reports[1-7] correlated and evaluated the results of pilot plant and laboratory research on 14 different processes.

In a summary paper[8] Peters, Kirby, and Higbie compared the operating cost of the more promising processes (see Table 4) for which brief descriptions follow:

TABLE 4. Operating Costs of Processes for 1000-Tons Per Day Alumina Plants

Process	Operating Cost $ Per Ton Alumina
Nitric acid	58
Sulfurous acid - caustic purification	62
Hydrochloric acid - isopropyl ether extraction	63
Lime-soda sinter with wet grind option	67
Lime-soda sinter with dry grind option	70
Sulfuric acid - electrolytic iron removal	80
Sulfuric acid - chemical iron removal	81
Potassium alum	94
Bayer process for bauxite	47

2. Nitric Acid. This process is based on the insolubility of iron in basic aluminum nitrate solutions. Dehydrated clay is digested with nitric acid to form a slightly basic aluminum nitrate solution in which iron is almost insoluble. The little iron that dissolves eventually precipitates during sedimentation, after which the silica and iron residue is separated by filtration. The solution is concentrated to crystallize aluminum nitrate monahydrate, leaving a basic aluminum nitrate mother liquor that is recycled to digestion. The crystals are washed with concentrated nitric acid and decomposed to alumina, nitrogen oxides, and water vapor in an indirectly fired kiln. Then the alumina is calcined to the alpha form in a second directly fired rotary kiln. To prevent the buildup of impurities in the recycled mother liquor, a small portion is withdrawn and evaporated to recover the nitrates which are decomposed to recover nitric acid.

3. Sulfurous Acid - Caustic Purification. The sulfurous acid caustic purification process is a preliminary treatment to remove silica before alumina is recovered by a modified Bayer process. Dehydrated clay is digested with sulfurous acid. The solution containing alumina and iron is filtered to remove the silica residue and autoclaved to precipitate a monobasic sulfite. A second autoclaving step decomposes the sulfite to alumina. Most of the iron also precipitates, resulting in a crude alumina, which is then treated with caustic as in the Bayer process.

4. Hydrochloric Acid. In the hydrochloric acid isopropyl-ether extraction process, clay (dehydrated by light calcination) is leached at atmospheric pressure with 20 percent hydrochloric acid to yield an aluminum chloride and silica slurry that is filtered to remove the silica residue. Virtually all the iron in the clay is dissolved and must be separated from the aluminum chloride solution to produce a satisfactory alumina. Proposed methods for separating the iron include solvent extraction using isopropyl ethers and/or

alcohols, using amines, or by repeated recrystallization from the solution by evaporation. After separation by centrifuging, the hydrated aluminum chloride crystals are calcined to alumina and hydrochloric acid that is recovered for recycling by condensing the vapor from the calcining kilns in fractionating columns. To date, it is not believed that this procedure has produced alumina that contains less than the acceptable industry maximum of 0.03 percent Fe_2O_3.

5. Sulfuric acid - Electrolytic Iron Removal. Dehydrated clay is leached with 40 percent sulfuric acid and the pregnant solution is separated from the clay residue. Iron is removed from the solution by electrolysis in mercury cathode cells. The iron-free solution is concentrated by evaporation and then filtered to remove the small remaining traces of silica. Further concentration of the solution results in crystallization of aluminum sulfate that is subsequently dehydrated and decomposed to α-alumina. The alumina is then purified by washing with 0.25 percent sulfuric acid, rinsed with water, and dried.

6. Sulfuric Acid - Chemical Iron Removal. This process is identical with item (5) above except that the iron in solution as ferric sulfate is precipitated as an iron-manganese complex by the addition of manganese sulfate and ozone rather than being removed from the solution by electrolysis.

7. Potassium Alum. Dehydrated clay is leached countercurrently with a solution containing sulfuric acid and potassium sulfate, and the resulting slurry is filtered to remove the siliceous residue. Alumina is dissolved as potassium alum and iron is dissolved as ferric sulfate. The ferric sulfate is reduced with sulfur dioxide to the ferrous form. The potassium alum is purified by crystallizing the alum from solution while leaving the ferrous iron in the mother liquor. The alum crystals are separated from the mother liquor by filtration and then redissolved with dilute potassium sulfate solution. After clarification, the purified solution is decomposed under pressure to form a

basic alum which is suitable for feed to multiple-hearth furnaces. Sulfuric acid and potassium sulfate are also formed in the autoclave and are recycled for leaching. The basic alum is decomposed to alumina, potassium sulfate, and sulfur oxides. The potassium sulfate is recovered by washing the alumina cake with water. The alumina is then dried and calcined.

8. Most Promising Acid Processes. In all these proposed acid processes there are three principal problems: separation of dissolved iron and aluminum salts, recovery of acid, and crystallization of an aluminum salt of sufficient purity to yield reduction-grade alumina.

An HCl extraction process is considered to be among those to approach the costs of the Bayer process on bauxite, for the following reasons:

a. HCl is an aggressive reagent. High extraction levels may be reached in a reasonable time at atmospheric pressure without supplying heat to the leaching step.

b. The silica content of clay is less soluble in HCl than in, say, H_2SO_4.

c. The solubilities of chlorides tend to increase with increasing temperature, thus minimizing scaling problems on heat-transfer surfaces.

d. Operation with a chloride system permits recovery of virtually all the acid consumed (including that used to leach iron and other impurities, except sodium, potassium, and calcium) through thermal decomposition at moderate temperatures, followed by condensation and absorption of the HCl in water.

e. The use of HCl permits separation of iron as the $FeCl_4$ complex, by solvent extraction.

f. Aluminum chloride forms only the hexahydrate when crystallizing from water at convenient temperature and pressure. Providing iron has been separated previously, it is easy to form pure crystals relatively uncontaminated with other soluble impurities. The concentration of other solubles can be controlled, in a continuous process, by withdrawing a bleed stream.

g. Aluminum chloride hexahydrate does not melt in its own water of crystallization. This makes thermal decomposition fairly simple.

A nitric acid extraction process also offers many of the advantages of the hydrochloric acid process.

a. HNO_3 is an aggressive reagent. High extraction levels may be reached in a reasonable time at either atmospheric pressure or under moderate pressure.

b. The silica content of clay is less soluble in HNO_3 then H_2SO_4.

c. The solubilities of nitrates tend to increase with increasing temperature, thus minimizing scaling problems on heat-transfer surfaces.

d. Through carefully controlled thermal decomposition at moderate temperatures, most of the nitric acid from both the aluminum and other impurity nitrates may be recovered by condensation and absorption in water.

e. The use of nitric acid permits the separation of iron by precipitation during the leaching step using a pressure step instead of a separate iron removal technique.

f. Aluminum nitrate may be crystallized from solution, leaving minor impurities in solution. Build-up of these impurities may be controlled in a continuous process by withdrawing a bleed stream.

9. Conclusions and Recommendations. The technical feasibility of producing near reduction-grade alumina by HCl extraction of clay has been demonstrated on a small scale. Probably in this process, as in the conventional Bayer process, there would be significant economies of scale--i.e., a 1,000 ton/day plant would be much cheaper per unit than one of 100 ton/day. This and other economic factors cannot be evaluated except by relatively large extensive pilot-plant testing.

This Panel recommends that the Bureau of Mines, with the financial help and cooperation of the domestic aluminum producers, choose a specific HCl process and a specific HNO_3 process and build and operate a pilot plant of from one to five tons/day. Hopefully, all of the producers would find it to their advantage to cooperate.

REFERENCES

1. Peters, F. A., Johnson, P. W., and Kirby, R. C., Methods for Producing Alumina From Clay - An Evaluation of the Sulfurous Acid-Caustic Purification Process: U.S. Bureau of Mines Report of Investigation 5997, 21 pp, 1962.

2. Peters, F. A., Johnson, P. W., and Kirby, R. C., Methods for Producing Alumina from Clay - An Evaluation of Five Hydrochloric Acid Processes: U.S. Bureau of Mines Report of Investigation 6133, 68 pp, 1962.

3. Peters, F. A., Johnson, P. W., and Kirby, R. C., Methods for Producing Alumina from Clay - An Evaluation of Three Sulfuric Acid Processes: U.S. Bureau of Mines Report of Investigation 6229, 57 pp, 1963.

4. Peters, F. A., Johnson, P. W., and Kirby, R. C., Methods for Producing Alumina from Clay - An Evaluation of a Potassium Alum Process: U.S. Bureau of Mines Report of Investigation 6290, 27 pp, 1963.

5. Johnson, P. W., Peters, F. A., and Kirby, R. C., Methods for Producing Alumina From Clay - An Evaluation of a Nitric Acid Process: U.S. Bureau of Mines Report of Investigation 6431, 25 pp, 1964.

6. Peters, F. A., Johnson, P. W., and Kirby, R. C., Methods for Producing Alumina from Clay - An Evaluation of Two Ammonium Alum Processes: U.S. Bureau of Mines Report of Investigation 6573, 47 pp, 1965.

7. Peters, F. A., Johnson, P. W., and Kirby, R. C., A Cost Estimate of the Bayer Process for Producing Alumina: U.S. Bureau of Mines Report of Investigation 6730, 23 pp, 1966.

8. Peters, F. A., Kirby, R. C., and Higbie, K. B., "Methods for Producing Alumina from Clay," Journal of Metals, October 1967.

C. Alkaline Processes for Low Grade Bauxites and Clays

1. General. No process has been devised that can produce Al_2O_3 more cheaply than the Bayer process that utilizes bauxite. This section treats low-grade bauxite, as defined in the previous section, and particularly those where aluminum silicates are present in large quantities. Because the usable processes are the same, whether the raw material is low-grade bauxite or clay, no distinction will be drawn.

Most alkaline processes available for aluminous ores were outlined by Edwards, Frary, and Jeffries in their book, "The Aluminum Industry" which was published in 1930. Their schematic outline is reproduced as Figure 4 and is nearly current. The Combination Process (see pp 38-40) could be added to this scheme although it amounts in principle to using two of the listed processes, i.e., digestion with caustic soda and furnacing with mixtures of alkali and alkaline earth carbonates and oxides, in sequence. If an appreciable amount of gibbsite or

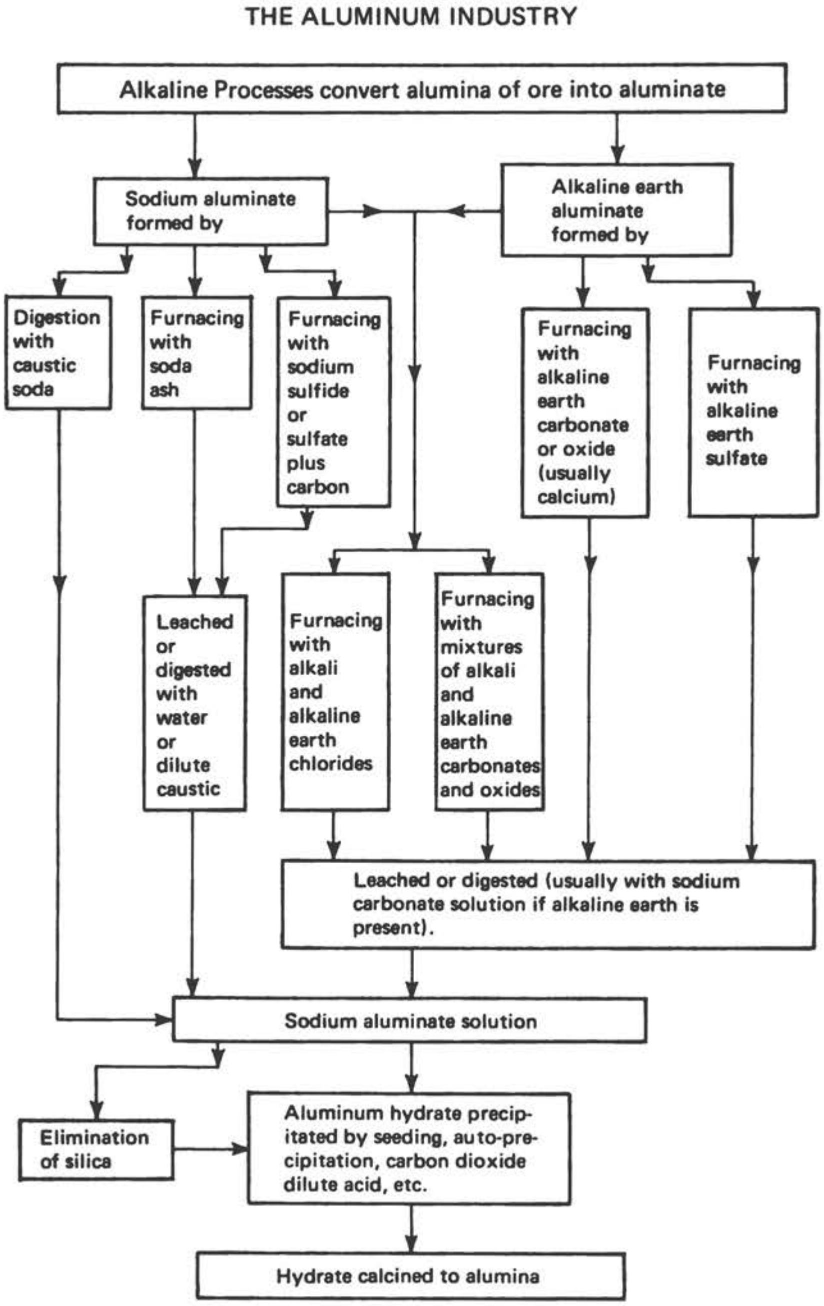


Figure 4. Outline of Unit Operations in Alkaline Processes for Producing Alumina

Source: "The Aluminum Industry," Edwards, Frary, and Jeffries, 1930.[1]

boehmite is present in the bauxite, the Combination Process is usually justified because recovery of a portion of the Al_2O_3 by the Bayer process reduces sinter fuel requirements and the amount of evaporation required per unit of Al_2O_3 produced.

2. Hydrothermic Lime Soda. Another development not shown in Figure 4 (USSR patent 108,917) is the digestion of aluminous materials in very high concentrations of NaOH at temperatures above 250°C. This is followed by crystallization of hydrated sodium aluminate for subsequent processing. Under the conditions of the digest, the addition of CaO is reported to cause the formation of $Na_2O \cdot 2CaO \cdot 2SiO_2 \cdot H_2O$ instead of sodium aluminate silicate so that Al_2O_3 recovery is in excess of 90 percent. Some Na_2O can be recovered from the washed red mud by a digest with additional CaO again at temperatures in the neighborhood of 250°C. Chemically, this process seems analogous to a lime soda sinter with sintering and leaching being replaced with two hydrothermal treatments.

3. Vereinigte Aluminium Werke. A third process which can be added is the Vereinigte Aluminium Werke process (Norwegian Patent 90811) in which clay or low grade bauxite is roasted at approximately 1000°C, then given an atmospheric digest in 20-30 percent NaOH. The digest time must be relatively short because the process depends on the rate of solution of the SiO_2 being greater than the rate of solution of alumina. The desilication reaction also proceeds to some extent during the digest. However, it is possible to dissolve more than half of the SiO_2 while dissolving 5-7 percent of the Al_2O_3. The same patent reports that a second leach with 10 percent NaOH will remove more of the SiO_2. The treated residue is extracted under European Bayer process conditions to recover Al_2O_3 and the leach solutions which contain SiO_2 are recausticized with CaO. The necessity for rapid separation of the residue from the caustic leach solutions requires filtration rather than sedimentation. With the operations of

(1) the second caustic leach, (2) removal of the residue after Bayer digestion, and (3) separation of the lime sludge from the recausticized leach liquors, the process involves a great deal of clarification, washing and evaporation. Digestion of the roasted ore calls for conditions not common in American technology.

In processing low-grade bauxites and clays, all processes that use only NaOH or sodium salts as reagents can be eliminated from consideration. These include the caustic digests, soda sinters, the Peniakoff (sinter with Na_2SO_4 and C) process. The conditions of these processes will solubilize the SiO_2 as well as the Al_2O_3. With only Na_2O present, the SiO_2 can be removed only as the desilication product resulting in uneconomic losses of Al_2O_3 and Na_2O.

Various processes have been proposed for the recovery of Na_2O from the desilication product by digests with CaO at temperatures ranging from the atmospheric boiling point to 350°C. From 4 to 5 pounds of CaO are necessary to recover one pound of Na_2O. The ratio of Na_2O value to CaO cost must be very high for the recovery to pay for the reagent used plus the costs of digestion, clarification and concentration. Further, since there is little Al_2O_3 recovery in this operation, it is not applicable to materials in which the reactive $SiO_2:Al_2O_3$ ratio is high.

4. <u>Lime Soda Sinter</u>. Development of a lime soda sinter process (Figure 5) began as long ago as 1902, when Adolph Kayser[2] obtained a patent on a process for separating alumina from silica. Early work on the lime soda sinter process was reviewed by Conley and Skow,[3] and Edwards, Frary and Jeffries The lime soda sinter process is one of the few alkaline processes that is in commercial use. The process is applicable to a wide variety of raw materials including clays and anorthosite. The Combination Process is a special case of the lime soda sinter in which the raw material is the red mud residue from Bayer digestion of low grade bauxite.

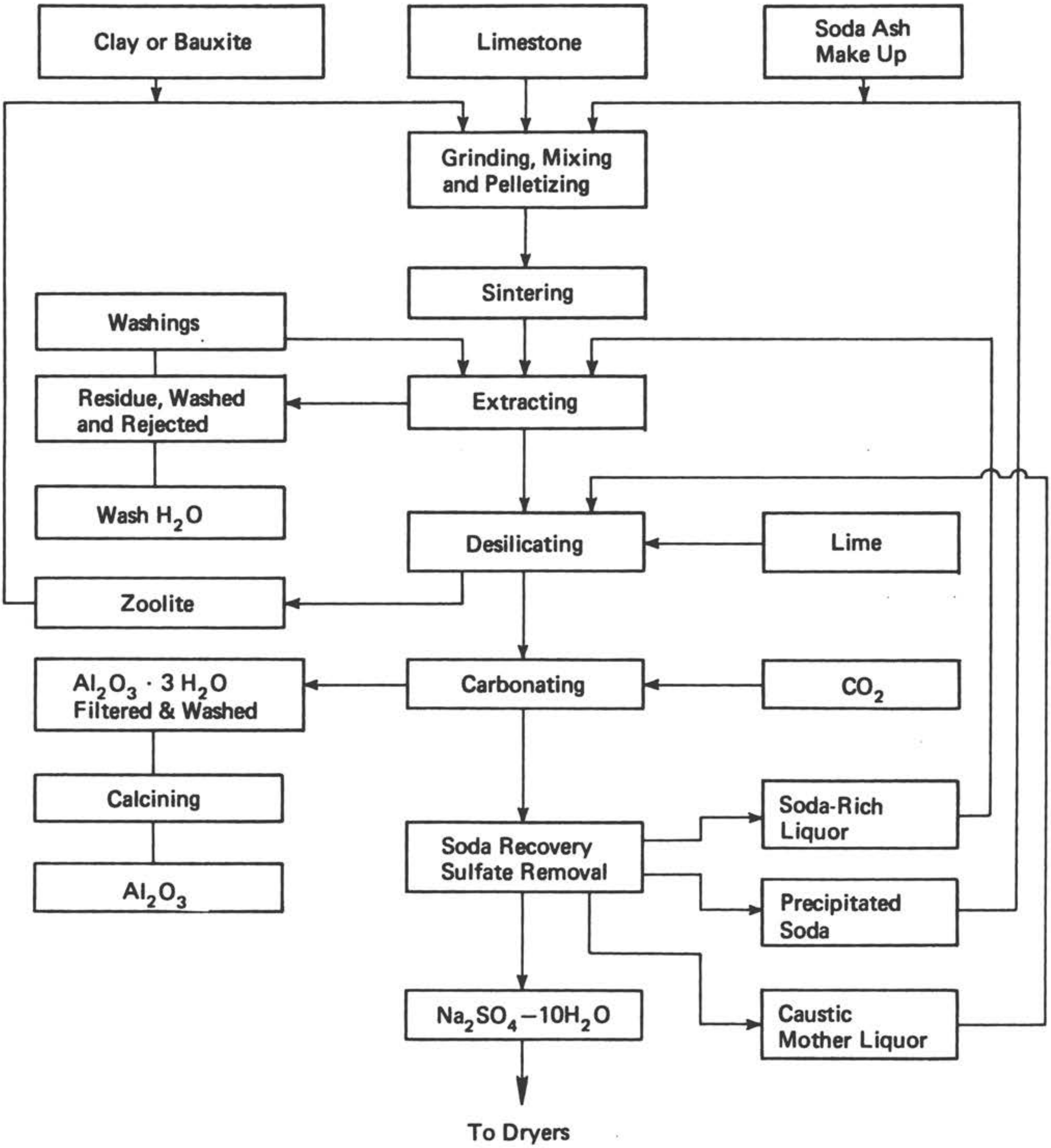


Figure 5. Flow Sheet of Lime-Soda-Sinter Process for Alumina

In the lime soda sinter process, the objectives are to convert the Al_2O_3 into soluble $NaAlO_2$ and the SiO_2 into insoluble $2CaO \cdot SiO_2$. To this end, a source of Na_2O, usually Na_2CO_3, is added so that the mol ratio $Na_2O:Al_2O_3$ is 0.8 to 1.2. The tendency is to use higher mol ratios when Fe_2O_3 is present in quantity.[4] This seems unnecessary since X-ray diffraction does not show the presence of sodium ferrate[13] and another investigation[5] shows no effect of Fe_2O_3 up to 24 percent in the raw material. The mol ratio of $CaO:SiO_2$ is in the range 2.0 to 2.2. There is consensus[6] that fine grinding of the raw materials is necessary for nearly complete reaction and subsequent high recovery of Na_2O and Al_2O_3. Recent laboratory work by the Bureau of Mines[6] has indicated that excess Na_2O and CaO, above that required for the alumina and silica, tend to cause gelation.

5. Combination. The mixed ground raw materials can be fed to the sinter kiln either wet or dry. In the Combination Process, a red mud slurry is fed and the mix granulates as it dries in the kiln. Firing temperatures are generally in the range 1100 to 1200°C[7] although some experimenters have used temperatures as high as 1350°C. Firing at sufficiently high temperatures is necessary to complete the reaction, to enhance extraction, and to prevent gelation of the mud during leaching; temperatures that are too high can result in formation of fusion rings within the kiln. The cooled sinter can be leached after dry grinding or during wet grinding. Generally from 2 to 3 pounds of water or a dilute solution of Na_2CO_3 is used per pound of sinter.

Gelation is the most feared condition in leaching. When it occurs, the leached mud becomes voluminous and retentive of process solutions. Filtration rates drop and extraction is very low. Nearly all sinter residues will gel,[8] but most rapid gelation takes place when composition control is faulty, when the sinter is underfired, when NaOH is present and when the sinter is finely ground. It can be slowed by use of higher concentrations of Na_2CO_3 in the leach or by the addition of sugar. Generally, operating conditions are controlled so that gelation will not occur in the time required for leaching and removal of the residue. Leaching can also be accompanied by other reactions[9] which form insoluble calcium aluminate compounds, result in hydrolysis of the $NaAlO_2$ to precipitate $Al_2O_3 \cdot 3H_2O$, or form desilication product scale. The leach solutions generally contain 80 gram/liter Al_2O_3 or more[4] and from 1 to 5 gram/liter SiO_2.

In recovering the Al_2O_3 from the leach liquor, the objective is to minimize the Al_2O_3 recycled to the sinter operation with the Na_2O and, yet, to meet the SiO_2 specifications of the product. In the Combination Process, this is not a problem because the material balance permits the Al_2O_3 to be precipitated in the Bayer process so desilication using a pressure digest is adequate. When the SiO_2 content of the raw material is high, no Bayer operation is possible so the Al_2O_3 must be precipitated by neutralizing the $NaAlO_2$ with CO_2. Herein lies a problem, since SiO_2 is also precipitated at a rate which increases as neutralization nears completion. Over the past 40 years, the permissible SiO_2 in Al_2O_3 for smelting has decreased from 0.08 percent[1] to about 0.02 percent. Meeting this recent specification is exceedingly difficult with carbonation. Removal of SiO_2 from $NaAlO_2$ solutions has been given a great deal of study. Elevated temperature digests, which use an excess of CaO, lower the SiO_2 sufficiently to permit a reasonable approach to specifications.[8] This does result in precipitation of insoluble calcium aluminates which may be recycled to the process feed. Control of the concentration, temperature and neutralization rate can be used to precipitate the Al_2O_3 in any form from a gel to "sandy."

There seems to be a sufficient amount of laboratory and pilot experience[10] on the lime soda sinter process to permit evaluation. There is no apparent reason to question the Bureau of Mines' evaluation[11] that shows the lime soda sinter process to be somewhat more costly on clay than the least expensive acid processes.

Alumina costs from the Combination Process are lower than costs from a lime soda sinter of clay because a major portion of the alumina is produced by the relatively low cost Bayer process. Further domestic exploitation of the Combination Process seems unlikely since the bauxite deposits that are large enough to support commercial operations are already being used. The economics of the lime soda sinter process could be improved if it were possible to produce and market cement from the residue. This hope seems rather forelorn because of the difficulty in removing all of the Na_2O from the residue, because of the very large quantities of cement that would be produced and because of the dependence of cement economics on utilization within about a 200-mile radius.

6. Lime Sinter. In the lime sinter process (Figure 6), limestone is charged to the process to convert the Al_2O_3 and SiO_2 to calcium compounds; $2CaO \cdot SiO_2$ is one target and the general mol range of $CaO:Al_2O_3$ is 1.5-1.8. Temperatures in lime sinter, 1300-1400°C,[12] are somewhat higher than those used in the lime soda sinter. In the Pedersen process,[13] the temperature is raised to effect fusion and the fusion can be accompanied by reduction of Fe_2O_3 and SiO_2. With proper composition control, the sintered and fused products can be largely self-comminuting due to volume expansion in a phase change on cooling. Material that does not readily decrepitate could be recycled advantageously to the sinter kiln feed.

The finely ground product is leached with relatively dilute Na_2CO_3 solutions to form $NaAlO_2$ and $CaCO_3$. Most of the SiO_2 remains insoluble. In leaching, excess NaOH and high concentrations should be avoided

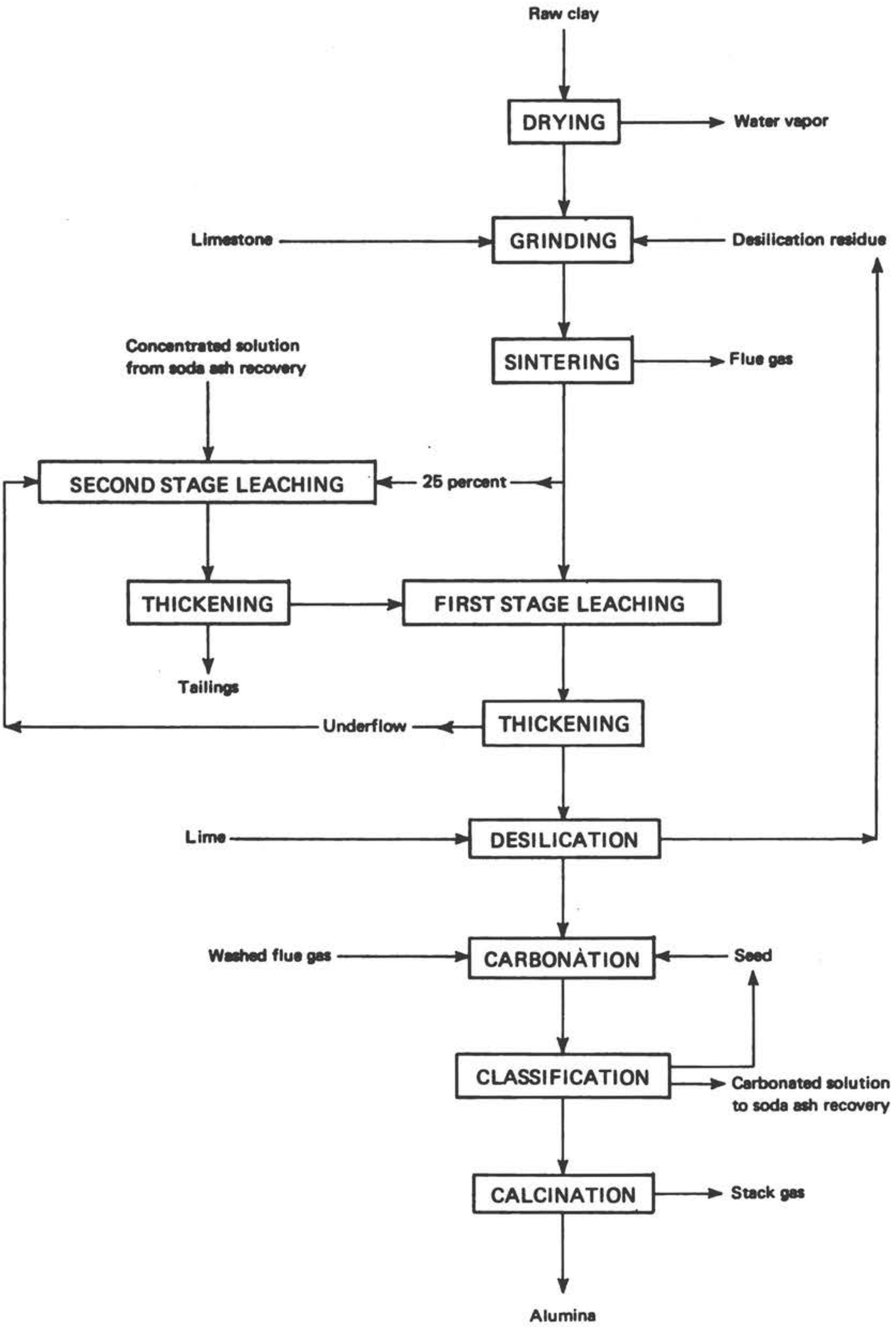


Figure 6. Lime Sinter, Double-Leach Process

Source: U.S. Bureau of Mines R.I. 7299, p. 5, Sept. 1969 so that the leaching reaction can proceed toward completion. Generally, the Al_2O_3 concentrations in the final leach solution are below 40 grams/liter. The SiO_2 concentrations are approximately 1.5 percent of the Al_2O_3.[12] Since the leach liquors from the lime sinter are less concentrated than those from the lime soda sinter, the absolute value of the SiO_2 concentration going to carbonation must be lower. Some investigators[13] who have used a two-stage leach, claim that the contact of the leach solution with an excess of sinter effects SiO_2 removal. Digests of the leach liquor with lime, parallel to those with the lime soda sinter, have been reported and one investigator[13] used calcined MgO in a boiling digest. After desilication, precipitation operations are very similar to those used in the lime soda sinter.

The recycling Na_2O used in the lime sinter process remains in solution so there is not as much evaporation required as in the lime soda sinter. This is more than counterbalanced by the increase in the amount of lime and fuel required; therefore, costs are higher.[14] Although the residue from the lime sinter could be readily usable in cement, there is a tremendous quantity of such material produced per unit of Al_2O_3.

7. Conclusions and Recommendations. In summary, the available experimental and pilot plant data on most of the alkaline processes appear sufficient to conclude that these processes cannot normally compete economically with acid processes. There may be some value in further work to demonstrate the conditions required for the VAW desilication process and the Russian hydrothermal process in which crystalline sodium aluminate is formed.

REFERENCES

1. Edwards, J. D., Frary, F. C., and Jeffries, Zay, The Aluminum Industry, "Aluminum and Its Production," New York, McGraw-Hill Book Company, vol 1, 1930, pp 146-147.

2. Kayser, Adolf, Process of Separating Alumina from Silica. U.S. Pat. 708,561, Sept. 9, 1902.

3. Conley, J. E., and Skow, M. L., Lime-Soda Sinter Process for Alumina from High-Silica Bauxites: Laboratory and Pilot-Plant Tests, U.S. Bureau of Mines, RI 4462, June 1949.

4. Suzuki, Takamura, Studies on Extraction of Alumina from Aluminous Raw Materials by the Soda-Lime Process in the Pilot Plant, Bulletin of the Government Chemical Industrial Research Institute, Tokyo, March 1950.

5. Lundquist, R. V. and Chardoul, N., The Desilication of Caustic Leach Liquors Containing Alumina, Bureau of Mines, RI 6100, 1962.

6. Ampian, Sarkis G., Lime Soda Sinter Process - Correlation of Reaction Products with Extractability of Alumina from Anorthosite, U.S. Bureau of Mines, RI 6933, April, 1967, 44 pp.

7. Copson, R. L., Walthall, J. H., and Highnett, T. P., The Extraction of Alumina from Clays by the Lime-Sinter Modification of the Pedersen Process, War Metallurgy Committee of National Academy of Sciences, National Research Council, Advisory to National Defense Research Committee of Office of Scientific Research and Development and Office of Production Research and Development of War Production Board, Serial No. W-103, Copy No. 24, April 1944.

8. Ervin, G., Blue, D. D., and Conley, J. E., Control of Gelation in Extraction of Alumina from Lime-Soda-Clay Sinters, U.S. Bureau of Mines, RI 3923, August 1946.

9. Lecis, P., and Guidi, A., Pyrogenic Attack of Bauxite, Soc. Montecatini Aluminium Div., Porto Marghera Venice (Italy), Via Delle Industrie 26, 1961.

10. St. Clair, Hillary W., Elkins, Douglas A., Shibler, B. K., Mahan, W. M., Merritt, R. C., Howcroft, M. R., and Hayashi, M., Operation of Experimental Plant for Producing Alumina from Anorthosite, U.S. Bureau of Mines, Bulletin 577, March 1949.

11. Henn, John J., Johnson, Paul W., Amey, Earle B., III, and Peters, Frank A., Methods for Producing Alumina from Clay - An Evaluation of Two Lime Sinter Processes, U.S. Bureau of Mines, RI 7299, Sept. 1969.

12. Grim, R. E., Machin, J. S., and Bradley, W. F., Amenability of Various Types of Clay Minerals to Alumina Extraction by the Lime Sinter and Lime-Soda Sinter Processes, State Geological Survey, Urbana, Illinois, 1945.

13. Klema, Friedrich, The Production of Metallurgical Alumina, Part II, Reprint from Mitteilungen des chemischen Forschungs institutes der Wirschaft Oesterreichs, Innsbruck, vol 3, No. 2, April 1949.

14. Cservenyak, F. J., Recovery of Alumina from Kaolin by the Lime-Soda Sinter Process, U.S. Bureau of Mines, RI 4069, May 1947.

BIBLIOGRAPHY

Cservenyak, F. J., Ruppert, J., Garen, D. E., Extraction of Alumina from High-Iron Bauxites - Pilot-Plant Tests Employing the Lime-Soda Sinter Process, U.S. Bureau of Mines, RI 4299, June 1948.

Frattali, F. J., Green, S. J., and McLendon, V. I., Recovery of Soda and Removal of Sulfate in the Lime-Soda Process for Alumina Production, U.S. Bureau of Mines, RI 4126, Sept. 1947.

Lundquist, R. V., and Singleton, E. L., Some Characteristics of Iron in the Lime Soda Sinter Process for Recovering Alumina from Anorthosite, U.S. Bureau of Mines, RI 6090, 1962.

Sherwin, R. S., Production of Alumina for Aluminum from Raw Materials other than Bauxite with Special Reference to Nepheline, Translated from Chemiker-Zeitung, July 1, 1937.

Strokov, F. N., Symposium on the Production of Aluminum Oxide and Alkalies from Nepheline by the Alkali Method, Translations of The State Institute of Applied Chemistry, (USSR) No. 29, p 5-272, 1936.

Peters, F. A., Kirby, R. C., and Higbie, K. B., "Methods for Producing Alumina from Clay - an Evaluation," Journal of Metals, October 1967.

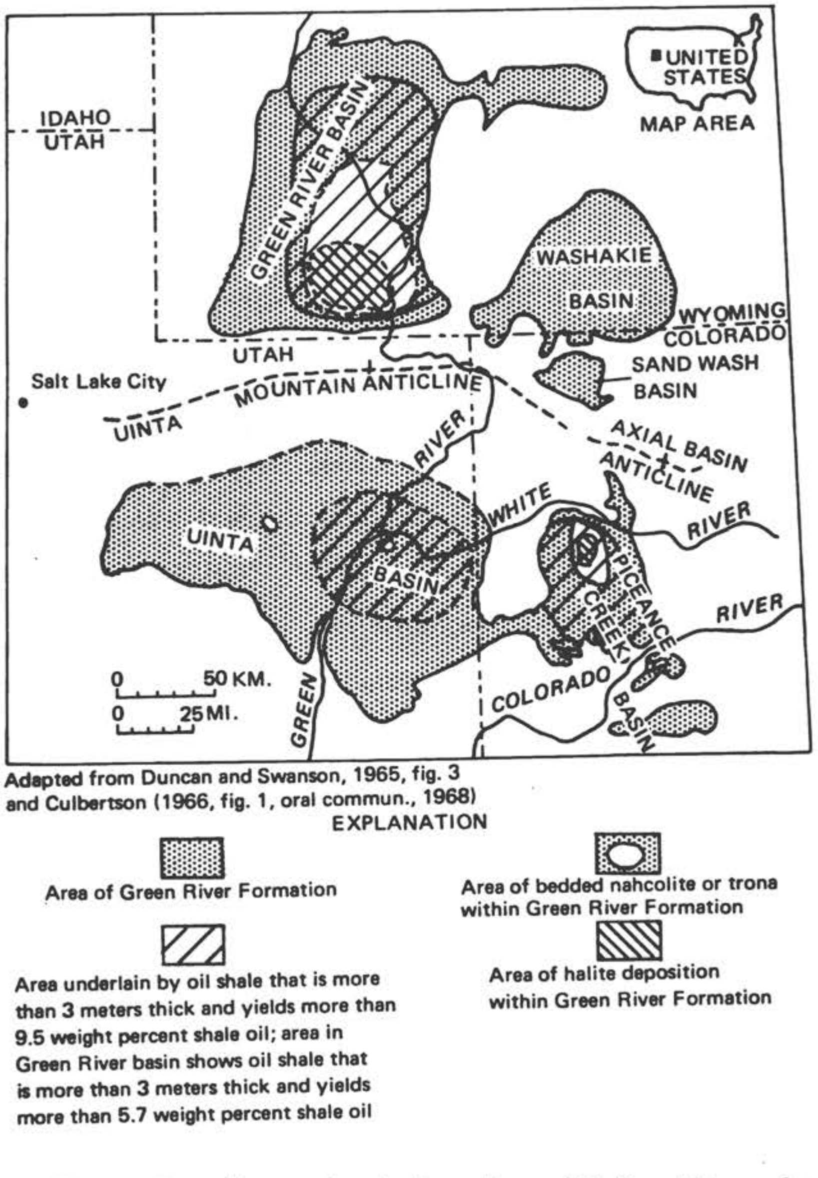
The Combination Process for Alumina, Junius D. Edwards Aluminum Research Labs. Tech. Publ. No. 1833 of Amer. Inst. of Mining and Metall. Eng. 11/29/44.

D. Dawsonite

1. General. Within the last four years potentially large deposits of sodium minerals, one of which contains aluminum, have been discovered in association with the deep oil shales of the Green River Formation of the western United States, principally in the Piceance Creek Basin of northwestern Colorado (Figure 7). Among the major minerals of interest are dawsonite [$NaAl(OH)_2CO_3$], nahcolite ($NaHCO_3$), halite (NaCl), trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), and shortite [$Na_2CO_3 \cdot 2CaCO_3$]. Because the dawsonite may constitute a vast new domestic source of alumina, it is pertinent to examine the nature and extent of its occurrence, the processes available for its conversion to Al_2O_3, and such economic and cost factors as are presently known.

These sodium minerals are currently the subject of preference right lease claims resulting from previously issued sodium prospecting permits and, until recently withdrawn, of locatable-minerals sodium mining claims. In partial support of these claims, a number of private companies have conducted preliminary laboratory and pilot plant research on alumina recovery from dawsonite. Since most of this research to date is understandably of a proprietary nature, it is necessary to rely, in part, upon private communications in order to assess the current state of dawsonite technology.

2. Occurrence. The geological occurrence of the dawsonitic-sodium minerals is treated in depth in Appendix A.



Adapted from Duncan and Swanson, 1965, fig. 3 and Culbertson (1966, fig. 1, oral commun., 1968)

Figure 7. Approximate Location of Saline Minerals in Green River Formation Oil Shales of Western United States

Source: "Potential Resources of Dawsonite and Nahcolite in the Piceance Creek Basin, Northwestern Colorado," Colorado School of Mines Quarterly 62, No. 3 (1967)

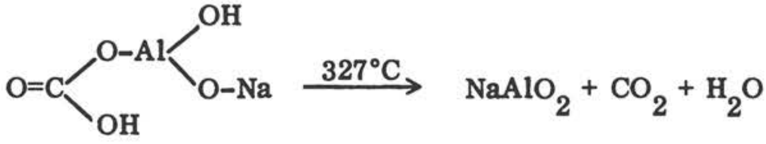
3. Recovery of Dawsonite. Because most dawsonite in the Green River Formation oil shale is intimately disseminated throughout the oil shale in finely-divided crystalline form, it does not lend itself readily to liberation and recovery by conventional ore dressing techniques (e.g., flotation). It is also not readily extractable, per se, by water, but can be extracted by dilute acid or base leaching.

In selecting a leaching agent, it must be recognized that fine-grained quartz, albite, potash, feldspars, dolomite, calcite, and small amounts of pyrite are also present in the saline zone together with coarser-grained nahcolite and, of course, oil shale organic matter. Dilute acid extraction is an effective laboratory analytical technique but, probably, this method of leaching would be uneconomical on a commercial scale. The high concentrations of associated basic minerals present would consume greater values of acid than the potential values of the recoverable products. In addition, complicated separation problems (alums, mixed salts, etc.) could be encountered. Therefore, an alkaline leach is the most attractive approach.

The oil shale organic matter in the deposit tends partially to coat and to protect the dawsonite and other minerals present from intimate contact with any leaching solution, thus reducing extraction efficiency. Therefore, it is desirable to first remove the organic matter either by calcination of the raw shale, or, preferably, by using a conventional oil shale retorting process which permits simultaneous recovery of valuable shale oil. In selecting a calcination or retorting temperature, careful attention must be given to the reactions of the dawsonite and other minerals under heat. At excessively high temperatures, the formation of insoluble aluminum compounds (oxides and silicates), glasses, etc., is likely. In addition, if retorting for shale oil is contemplated, the added heat requirements resulting from endothermic decomposition of carbonates, etc., would be economically unattractive.

By differential thermal analysis and differential scanning calorimetry, dawsonite has been shown to exhibit two large endothermic reactions in the 300-400° C temperature range. In a recent study by Denver Research Institute,[1] two separate reactions are proposed for the two different forms of "dawsonite" that are believed present. The two forms of dawsonite [both $NaAl(OH)_2CO_3$] are proposed to be as follows: A bicarbonate form (Dawsonite I), decomposing at 327°C (621°F) according to the reaction

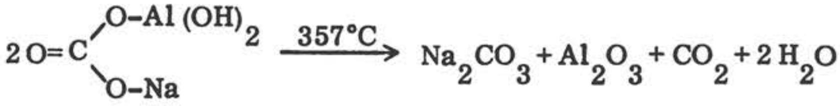
(a)



(Dawsonite I)

to produce soluble sodium aluminate; and a conventional carbonate form (Dawsonite II), decomposing at 357°C (675°F) according to the reaction

(b)



(Dawsonite II)

to yield an insoluble aluminum oxide.

If a dawsonite-containing oil shale is heated above 400°C to remove the organic matter, and the resulting denuded shale then extracted with a dilute alkali* (e.g., 1 M NaOH), a portion of the original aluminum present is made soluble and appears in the leach extract. The amount of solubilized aluminum is a function of both the temperature of calcination and the alkali concentration. A typical calcination temperature vs. percent aluminum solubilized curve is shown in Figure 8 when 1 M NaOH is employed as the subsequent leaching agent.[2]

It is noted in Figure 8 that a maximum of 61 percent of the original aluminum present in the calcined shale is solubilized, at a calcination temperature of 500°C (932°F). (In a second test, reported by a major aluminum company laboratory, percent extraction is reported to be 64 percent.[2] Assuming that primarily the dawsonite aluminum is rendered soluble, dawsonite I (the bicarbonate form) is suggested as being converted by reaction (a) to sodium aluminate and, subsequently, solubilized by the one molar caustic.

Whether or not the above mechanism is applicable, 500°C appears to be a useful optimum calcination temperature for soluble aluminum production, if 1 M sodium hydroxide is used as the subsequent leaching agent. More importantly, 500°C (932°F) is coincidentally a satisfactory temperature for the retorting of the oil shale to obtain oil. Thus, conventional shale retorting followed by an alkaline leach is suggested as a potential initial sequence for aluminum recovery. The resulting sodium aluminate solution would be acidified by carbonation and the $Al(OH)_3$ obtained calcined to cell-grade alumina by conventional techniques. Thus:

$$\text{(c)}\quad 2\ NaAlO_2 + CO_2 + 3\ H_2O \rightarrow Na_2CO_3 + 2\ Al(OH)_3$$

---

*With more concentrated alkali (e.g., 2.5 M NaOH) alumina recovery is poor, the silica present is attacked, and carbonation of the caustic by dolomite occurs, thus making the extract unattractive for subsequent processing by the Bayer process.[2]

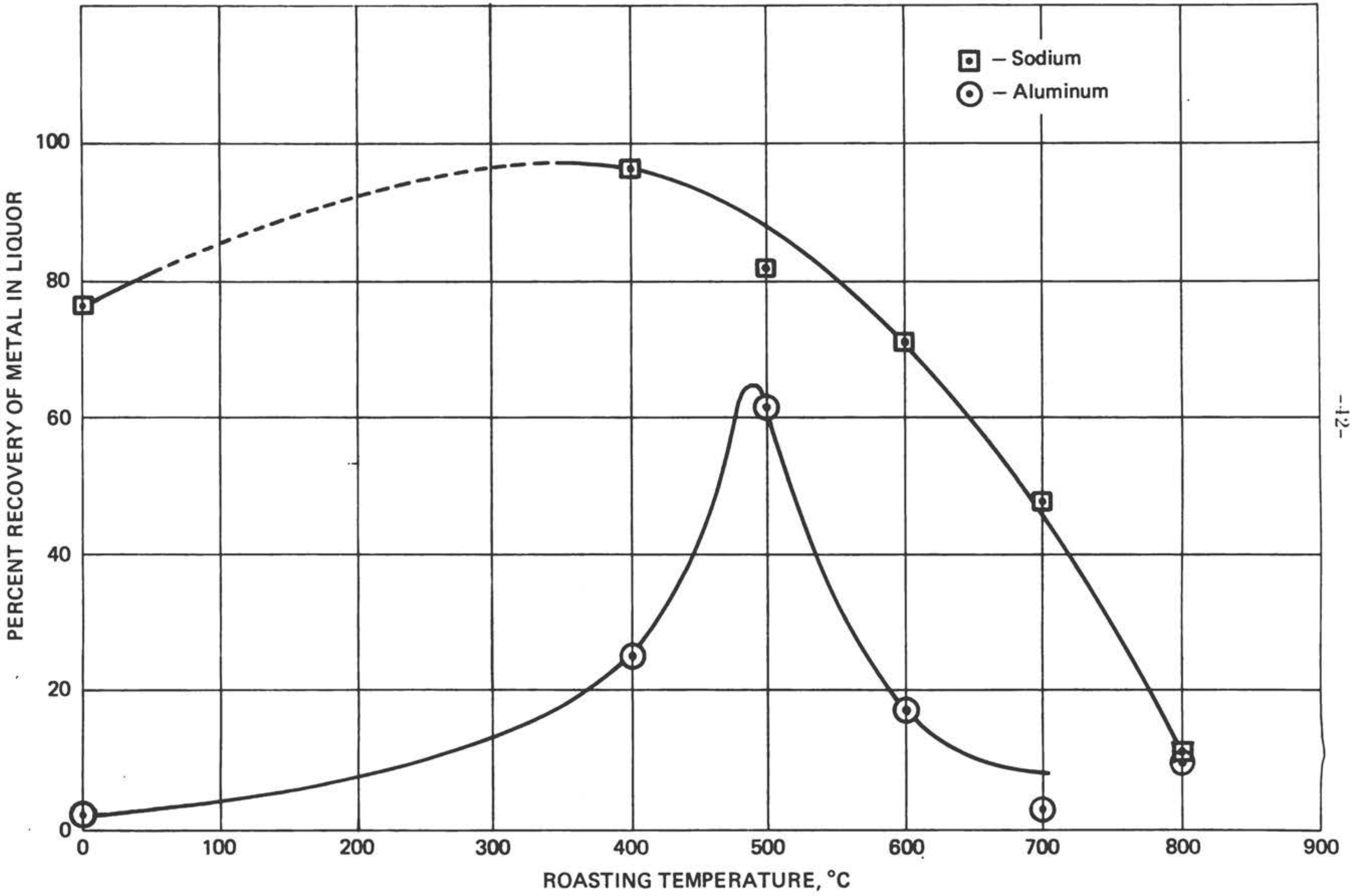


Figure 8. Effect of Retorting (or Calcination) Temperature on Solubility of Aluminum in 1M NaOH Leach Liquor

Source: C. H. Prien, private communications to the author

(d) $2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

Several potential improvements in the above processing sequence have been described in a recent patent[3] that has been assigned to the Oil Shale Corporation (Tosco). The dawsonite-bearing oil shale is first retorted at temperatures in the conventional 750-975°F range. Then the spent shale is roasted in an oxidizing atmosphere at 1100°F-1300°F in order to remove residual "carbon" and to produce sodium aluminate. The spent ash-sodium aluminate mixture, so obtained, is then leached with a 4 percent soda ash solution, resulting in a 75 percent extraction of soluble alumina. If 0.2 to 1.0 percent caustic soda is added to the soda ash leaching solution, extraction efficiency may be as high as 90 percent, but unwanted dissolved silica increases substantially.

The required soda ash can be obtained by recycling the sodium carbonate solution produced as a result of subsequent carbonation of the sodium aluminate (reaction (c) above). Lime can be added to the recycle solution, if desired, to produce NaOH by reaction with part of the soda ash. Therefore, the entire process appears to offer several attractive advantages over conventional caustic leaching.

An interesting modification in the treatment of the dawsonitic shales has been offered by Hite,[4] in a recent patent assigned to the Secretary of the Interior. He proposed adding excess sodium mineral salts (e.g., nahcolite, trona, shortite, gaylussite, or halite) to the raw dawsonite oil shale prior to retorting. (Most of these salts are already naturally present in the saline shale deposits). By these additions, the pyritic and organic sulfur is claimed to be converted to sodium sulfate with a resulting increased water solubilization of the aluminum present and a substantial reduction (at least 50 percent) in the sulfur content of the resulting shale oil. Both claims are of potential commercial significance, if economically viable.

Certain zones of the dawsonitic shales also contain up to 20 percent of nahcolite, which is present in a brittle, crystalline state. Although this salt could be separated by a hot water extraction (80°C) prior to retorting, a more economical method appears to be available. Because of its friability, nahcolite tends to concentrate in the fines when the shale is ground and screened. However, the primary separation is by no means complete, even when the raw shale is ground to minus 35-mesh.[6] Further treatment of the enriched fraction would be required if high soda ash recovery, per se, were contemplated.

The enriched crude nahcolite fraction might, of course, be sold as such. Also, crude nahcolite, which is selectively mined from nahcolite-rich saline horizons of the Piceance Creek Basis, has been suggested as an agent for the removal of sulfur oxides from power plant and smelter stack gases.[5, 6]

Mention should be made at this point of a number of current projects to retort oil shale in situ, using various fracturing techniques, including a nuclear detonation (Project Bronco), followed by an underground "fireflood" process. At the present state of in situ technology, probably, a great part of the sodium and aluminum values might be lost, if such in situ processing were conducted in the dawsonitic shales. The high temperatures involved would convert the aluminum to a form not readily extractable. Solution mining of the sodium and aluminum values has been suggested but technical and economic problems are still formidable.

4. <u>Economic Factors</u>. At the present time, processing of the major portion of the dawsonite resources appears to be dependent upon the future development of a U.S. oil shale industry.* Since future petroleum needs probably will require the processing of large tonnages of oil shale in the next few decades,

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*The same is not necessarily true of the recovery of nahcolite either for its proposed use, as mined, for SO removal from stack gases, or for subsequent soda ash production.

the prospects appear favorable for the existence of a by-product alumina industry from oil shale dawsonite. While the average dawsonite content of the shale may be only 12 percent, large tonnages of dawsonitic spent shale will be produced. Laboratory data indicate that at least 65-75 percent of the available alumina is recoverable by currently known techniques. Even at 65 percent, there are present in the Piceance Creek Basin alone up to 6 billion tons of potentially extractable alumina from the 27 billion tons of estimated dawsonite present.

If 1,000,000 bbl/day of shale oil were eventually to be produced from the deep, dawsonitic shales of the Piceance Creek Basin by 1985, apparently up to 40,000 tons/day of alumina (14 million tons/year) could be obtained as a by-product. Thus, this source alone could theoretically satisfy over 50 percent of the projected U.S. demand for aluminum in 1985.

The flowsheet for a completely integrated industry, in which dawsonitic oil shale is processed to recover shale oil, alumina, nahcolite, and soda ash, has been proposed by Cameron and Jones for Wolf Ridge Minerals,[5] assuming 77 percent recovery of caustic soluble alumina, (Figure 9).

In a variation of the previous flowsheet, spent shale from oil shale retorting is proposed to be burned in a combustion plant to remove the residual carbon (and produce power) and, then, to be leached with an alkaline solution to recover soluble alumina. Representative costs and income have been calculated for this processing sequence in a plant treating 77,650 tons of mined rock per day, recovering 2,300 tons/day of alumina (70 percent recovery), and generating 142,000 kW of power. Presumably, the original mined rock would also contain 15 percent $NaHCO_3$ as nahcolite and would be calcined to recover 5,880 tons/day of soda ash (80 percent recovery).

The capital investment and annual operating costs (330 days/year) for this plant are estimated to be as follows, assuming no charge for spent shale.[2]

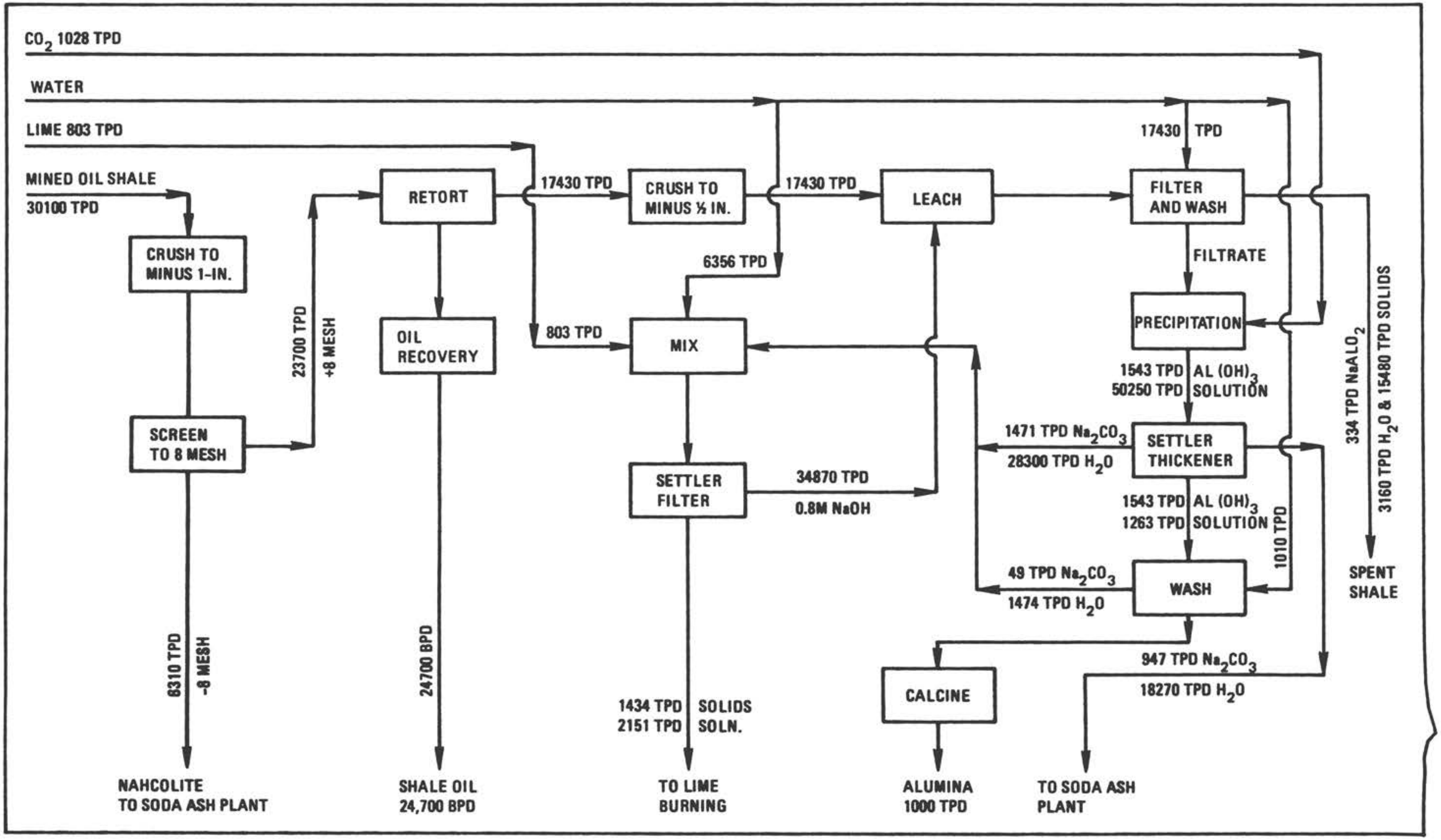

Figure 9. Proposed Flowsheet for Recovery of Saline Minerals (Including Dawsonite) from Piceance Creek Basin Oil Shales

Source: Nielsen, I., Engineering Mining Journal, Jan. 1969

	(Millions of Dollars) Capital Investment	Annual Operating Costs*
Spent Shale Combustion Plant	36	2.9
Alumina Recovery Plant	66	12.8
Soda Ash Plant	81	8.6
Totals	183	24.3

*Exclusive of depreciation and interest.

The annual gross sales and "net" income from the three products of this plant are estimated to be as follows:

	(Millions of Dollars) Gross Sales	Operating Costs	Net Income
Power (@ 7 mils/KWH)	7.8	2.9	4.9
Alumina (@ $45/ton)	34.4	12.8	21.6
Soda Ash (@ $10/ton)	19.4	8.6	10.8
Totals	61.6	24.3	37.3

It is recognized that the figures are order of magnitude estimates only. Nevertheless, apparently adequate incentive exists to consider the dawsonitic oil shales as a potentially valuable future source of nonbauxite alumina. Therefore, further research on this natural resource would appear to be amply justified, even though the extractable Al_2O_3 content of these shales is very modest in comparison to bauxite.

5. Protection of the Environment. The environmental control problems of a future dawsonite-alumina industry are primarily those of the integrated oil shale industry of which it will be a part. In addition, there will be those added pollution problems which are introduced in the subsequent leaching and recovery processes. In all cases, compliance with the regulations of the Environmental Quality Control Act of 1970 will be an obvious requirement.

The modern oil shale mining and retorting processes, currently under development, provide for adequate air, water, and solid-waste pollution safeguards as a matter of proper, economical engineering design. These safeguards include control of pollution from such sources as the dust in mining and crushing, stream pollution resulting from mining, retorting and subsequent partial refining and any air pollution (noxious gases, dust, etc.) which might accompany the retorting of the shale or the roasting of the dawsonite.

The most obvious environmental control problems are those involving the stockpiling of the spent shale prior to dawsonite roasting and the disposal of the spent shale after alumina recovery. Certain plant sites will permit the creation of limited dump areas in nearby gullies and canyons. These will be adequately dammed, drained, and replanted with native vegetation. However, as the industry grows of necessity, a major portion of the waste (denuded shale) must be returned to the underground mines from which it was taken. This will involve proper scheduling of the mining operations, acceptable techniques of waste compaction, and protection against any leaching due to possible underground aquatization.

The solubilization of the roasted dawsonite and its subsequent carbonation to recover alumina involve industrial chemical processing techniques for which adequate anti-pollution safeguards are already part of normal modern industrial practice. Indeed, the necessary basic engineering techniques already exist for proper environmental control throughout the entire oil shale-dawsonite processing sequence. Such pollution control will obviously add to overall processing costs. However, this is recognized by industry as being a legitimate item that must be included in the overall economics of alumina manufacture from dawsonite.

6. Conclusions and Recommendations. A second source of alumina worthy of serious consideration and more extensive research is the dawsonite deposits associated with oil shales in the Colorado-Wyoming-Utah area. The probable resources of dawsonitic oil shale in the Piceance Basin of Colorado alone are more than adequate incentive to investigate this potential domestic source of alumina. Order of magnitude cost estimates indicate that production costs might be attractive, even though the extractable alumina content is very modest.

Therefore, the Panel recommends that the Bureau of Mines expand its present research program on dawsonite. The program should include detailed mineral surveys of the extent and richness of the deposits, the technical variables affecting various recovery processes, and the economics of alumina production in relation to the sodium and oil industries with which it would be associated.

At the present state of technology, it is likely that a great part of the commercial value of the dawsonite shale might be lost if nuclear in situ processing were conducted.

REFERENCES

1. Schmidt-Collerus, J. J., and Hollingshead, R. D., "Investigations Into the Nature of Dawsonite in the Green River Formation," Colorado School of Mines Quarterly 63, No. 4, 143-167 (1968).

2. Prien, C. H., private communications to author.

3. Hall, R. N., and Haas, F. C. (to Oil Shale Corp.), U.S. Patent No. 3,510,255 (May 5, 1970).

4. Hite, R. J., (to Secretary of Interior) U.S. Patent No. 3,481,695 (Dec. 2, 1969).

5. Nielsen, I., Engineering Mining J., January 1969, p 57-60.

6. Chemical and Engineering News 47 (No. 23), 39 (June 2, 1969).

E. Aluminum from Aluminum Phosphate Rock

1. General. The Florida phosphate deposits are another potential raw material for the production of alumina. The leached zone, as it is called, contains 4 to 20 percent alumina and the deposit extends over several hundred square miles. At the present time, phosphate is produced from this material and the alumina is discarded with the tailings.

2. Geology. In Florida, the large phosphate deposits are overlain by two somewhat distinct zones. The surface layer is sandy soil, ranging in thickness from zero to 15 feet. The second layer, also ranging up to 15 feet in thickness, is variously called the leached zone, transition zone, or bottom clay. Beneath this is the matrix that consists of calcium phosphate pebbles embedded in clay and sand and is the phosphate ore. The leached zone is the largest deposit of aluminum phosphate in the United States. Since it extends over several hundred square miles, it may be considered to be a potential source of aluminum.

Table 5 gives the range and typical analyses for leached zone ore. Except where there is obvious contamination with calcium phosphate, the P_2O_5:Al_2O_3 ratio is about 0.85. Approximately 90 percent of the silica is present as quartz. The major aluminum phosphate minerals are wavellite, pseudo-wavellite, millisite and crandallite. Contaminants, besides quartz, are fluorapatite, kaolinite and goethite. Small quantities of fluorine and uranium which occur in the aluminum phosphate rock are of considerable interest.

TABLE 5. Analyses of Florida Leached Zone Ore

	Range in Percent	Typical Percent
Al_2O_3	4 - 20	13
P_2O_5	4 - 25	11
SiO_2	30 - 70	55
CaO	4 - 10	6
Fe_2O_3	1 - 6	3
F	0.5 - 1.7	0.9
LOI	5 - 15	8
U	0.01 - 0.03	0.02

3. Mining. Current strip mining procedure is to discard both upper layers when removing the overburden above the calcium phosphate matrix. This practice further dilutes the aluminum phosphate and would make alumina recovery more costly, if not impossible. If aluminum were to be recovered from the leached zone, it probably would be done in two stages with both aluminum and phosphate as products. This implies a relationship between the production of alumina and the production of phosphate. Some beneficiation of the leach zone can be accomplished by removing the coarser fraction. However, a clean separation is virtually impossible because some of the aluminum phosphate is as coating on the quartz grains.

4. Processing. The literature on processing leached zone material is sparse. The acid processes that have been attempted are similar to the acid processes used on clay but with two important differences. Generally, the acid solution is extracted with phosphate esters in kerosene for recovery of the uranium. There is also a recovery of a mixed fertilizer containing the phosphates in the leached zone ore. Alumina recovery is by hydrolysis in a pressure digest or by crystallization and decomposition of an aluminum salt. The ammonium alum has received more attention than any other salt. The phosphates are recovered by evaporation of the process solution.

In alkaline processing, better recovery of uranium can be effected by a digest of the leached zone rock in a solution of Na_2CO_3 than by an initial treatment with NaOH. The Na_2CO_3 digest frees the aluminum phosphate from the surface of the quartz so that the slurry can be beneficiated by separating on the basis of size. The beneficiated slurry can be attacked by a caustic digest or a soda sinter. In either case, sufficient Na_2O must be present to form both $NaAlO_2$ and Na_3PO_4. Recoveries of both Al_2O_3 and P_2O_5 are high. Separation can be effected by concentration and cooling to remove the sodium phosphate salts. Al_2O_3 is recovered by carbonation of the mother liquor. The requirement for carbonation gives some advantage to a soda sinter over an NaOH digest. If the Na_3PO_4 concentration of the aluminate solution is under 10 grams/liter, it is possible to precipitate $Al_2O_3 \cdot 3H_2O$ essentially free of P_2O_5. Also, the P_2O_5 can be removed by treatment of the solution with calcium compounds, such as the hydroxide or the aluminate.

Recovery of values from the crude Na_3PO_4 salts is difficult. First, the market for such salts is limited and, second, the salts are contaminated with $2Na_3PO_4 \cdot NaF \cdot 19H_2O$. After carbonation, the salts can be separated into NaF, Na_2CO_3 and Na_2HPO_4.

5. Economics. It will be impossible to treat the leached zone rock as a source of Al_2O_3 alone. It is also unlikely that economics will permit a process based on Al_2O_3 and P_2O_5. Interest in the leached zone diminished almost to zero in the late 1940's and early 1950's when the price of uranium dropped, following discovery of richer ores. The alkaline processes would bear a particularly heavy burden since even a small alumina plant would produce a sizable fraction of the sodium phosphate requirements for the United States. Without using mineral acids and producing undesirable sodium salts, it is impossible to go to a $Na_2O:PO_4$ ratio beyond that of Na_2HPO_4 toward salable phosphate salts. If an apatite is precipitated, some additional treatment is necessary in order to make the P_2O_5 readily soluble in standard fertilizer tests. The phosphate products from acid processes must compete with products from existing operations without any apparent economic advantage. These economic factors, together with the necessity of mining in conjunction with pebble phosphate production, leave the aluminum phosphate picture gloomy unless special circumstances should appear.

6. Conclusions. The production of alumina from aluminum phosphate rock does not appear to be economically feasible even if P_2O_5 were recovered as a by-product. Only increased return from potential additional

by-products, such as uranium and cement ingredients, could change the economic outlook.

BIBLIOGRAPHY

1. Beja, Maurice, and Vincent, Jean, "Treatment of aluminum phosphates," French Patent 1,158,823, June 19, 1958.

2. Dugger, G. L., Adams, J. B., and Bart, Roger, "Digestion and Filtration of Leached Zone in Pilot Plant," U.S. Atomic Energy Comm. RMO-2044, 35 pp (1955).

3. Huber, Hans, and Rohlfs, Hans A., "Alkali phosphates and alumina from phosphates containing insoluble impurities," German Patent 963,152, May 2, 1957.

4. Jardin, Louis, "Alumina and trisodium or tripotassium phosphate," French Patent 1,198,093, Dec. 4, 1959.

5. McCullough, Robert F., and Adams, Joseph B., "Recovery of alumina, uranium oxide, and phosphates from low-grade phosphate ore," U.S. Patent 2,894,809, July 14, 1959.

6. McCullough, Robert F., "Processing of high-aluminum phosphate ore," U.S. Patent 2,905,526, Sept. 22, 1959.

7. Milliken, Thomas H. Jr., "Alumina and Phosphates from Phosphate Rock," U.S. Patent 2,817,578, Dec. 24, 1957.

8. Obert, Fred N., and LeBaron, Ira M., "Concentrating phosphate ores with recovery of alumina and uranium oxide," U.S. Patent 2,868,618, Jan. 13, 1959.

9. Piros, Robert J., "Recovery of alumina, phosphates, and uranium from phosphate ores," U.S. Patent 2,767,046, Oct. 16, 1956.

10. Porter, John L., "Extraction of alumina from aluminum phosphate ores," U.S. Patent 2,812,239, Nov. 5, 1957.

11. Porter, John L., "Calcium aluminate and alumina from phosphate ores," U.S. Patent 2,903,338, Sept. 8, 1959.

F. Anorthosite

1. General. Anorthosite has long been considered by many as a possible raw material for the production of alumina. The material may be defined as a soda-lime feldspar igneous rock composed of variable amounts of albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). A number of large deposits exist in the United States, and the material has a very uniform composition making it an attractive raw material. Satisfactory alumina can be produced from anorthosite using the lime-soda sinter process. With this process, the known major technical problem is gelation in the leaching circuit. Recent laboratory work by the U.S. Bureau of Mines appears to have solved this problem.[1] On the other hand, anorthosite is a hard rock that would be costly to mine, and the lime-soda sinter process is more expensive than a number of acid processes for treating clay.

2. Availability. Total U.S. deposits are estimated at 599 billion tons averaging 27 percent alumina. Large deposits are located in California, Idaho, Montana, New York, Wyoming, and other states. A summary describing anorthosite deposits is given in the Bureau of Mines Information Circular 8335 "Potential Sources of Aluminum."[2]

3. Processing. The lime-soda sinter process is the most satisfactory method for producing alumina from anorthosite. Other processes have proven expensive or have not produced a reasonable alumina yield.

One large scale plant using the lime-soda sinter process was built near Laramie, Wyoming, during World War II. In 1945, the Defense Plant Corporation terminated construction of this 50-ton-per-day plant before its completion. In 1952, the Bureau of Mines modified the plant and operated it on an experimental basis. Although many variations of the lime-soda sinter process exist, only those considered in the Bureau of Mines evaluation[3] are presented in this report.

The lime-soda sinter process described in this report has two options—dry grinding of the raw materials, and the sinter and wet grinding of the same. In either option, anorthosite is sintered with limestone and soda ash to convert the alumina to sodium aluminate and to convert the silica to dicalcium silicate. The sintered product is leached with a dilute sodium carbonate solution to dissolve sodium aluminate from the sinter. The resulting slurry is processed to separate the residue from the leach liquor. This pregnant solution (leach liquor) is treated with lime in autoclaves to precipitate dissolved silica which is removed by settling and filtration. The desilicated liquor is carbonated to precipitate alumina trihydrate which is separated from the liquor, washed, and calcined to produce α-alumina.

4. Economics. The economics of recovering alumina from anorthosite are shown in Appendix B.

5. Conclusion. The production of alumina from anorthosite is not economically feasible at the present time.

REFERENCES

1. Ampian, S. G., Lime-Soda Sinter Process - Correlation of Reaction Products With Extractability of Alumina From Anorthosite; U. S. Bureau of Mines Report of Investigations 6933, April 1967, 44 pp.

2. U.S. Bureau of Mines, Potential Sources of Aluminum: U.S. Bureau of Mines Information Circular 8335, 1967, 148 pp.

3. Johnson, P. W., and Peters, F. A., Methods for Producing Alumina From Anorthosite - An Evaluation of a Lime-Soda Sinter Process: U.S. Bureau of Mines Report of Investigations 7068, 1968, 42 pp.

G. Alumina from Copper Leach Solutions

1. General. The recovery of copper from acid mine waters has been an established practice of great antiquity. In recent years, there has been increasing use of dilute sulfuric acid solutions to leach dumps of low grade copper bearing material or old mine workings. The copper is recovered from the solutions by precipitation on iron or by solvent extraction methods. The solutions also contain other metallic ions including aluminum, so an interest has developed in the possibility of recovering other metals in addition to the copper.

2. Extraction by Copper Leaching Solution. The rapid increase of the use of acid-leaching methods for the recovery of copper from waste dumps and low-grade ores represents a possible source of alumina. The solutions circulated per day at the Kennecott Copper Company properties are estimated to contain 1,000 tons of alumina. Obviously, this is an equilibrium condition reached after many cycles of copper leaching and precipitation. It would be difficult to predict accurately the daily amount of recoverable alumina, if the solutions were treated to precipitate part of the aluminum content during each cycle. However, precipitation by means of pressure hydrolysis yields a relatively high acid solution that upon passage through the dumps would presumably extract appreciable amounts of new aluminum content each cycle.

A serious consideration of this possibility on the part of the Kennecott Copper Company is evidenced by two patents[1,2] issued on April 1, 1969. The first patent refers to a continuous process for removing multivalent impurities from copper-bearing leach solutions. It states that acid-sulfate leach solutions, contaminated with relatively high concentrations of iron and aluminum, are subjected to elevated pressure and temperature conditions to cause the precipitation (due to hydrolysis) of both iron and aluminum precipitates and the regeneration of sulfuric acid. The precipitate may be processed for the recovery of iron, aluminum, or other valuable constituents. The second patent refers specifically to a process of producing high-purity alumina from aluminum-bearing acid sulfate solutions. These solutions are heated in the presence of sodium and/or ammonium salts at autogenous pressure to hydrolyze the aluminum present and to form a granular alunite precipitate. The precipitate is calcined to form a crude aluminum product that is digested in a strong caustic solution and then is purified in accordance with the Bayer process to produce high purity alumina.

D. R. George and others[3] in the Bureau of Mines have suggested that 2,000 tons of alumina per day may be available from the operations of 14 copper mines in the U.S. These figures are conjectural until further research determines the rate of leaching of aluminum from the waste dumps and the extent to which the concentration of aluminum in the solutions is controlled by equilibrium conditions.

According to these workers, much of the chemistry of the process for recovering aluminum from leach solutions is identical to that previously developed for producing alumina from clays. George and co-workers proposed a solvent-extraction method in which aluminum is extracted from the acid-sulfate solutions with a kerosene solution of an alkyl phosphoric acid. Then, the aluminum is stripped with 6-8 N HCl to yield a solution of aluminum chloride, rich in aluminum and depleted in H. The aluminum chloride strip solution is gassed with HCl to restore the concentration of free acid to 6-8 N. Simultaneously, most of the aluminum is selectively precipitated as crystalline $AlCl_3 \cdot 6H_2O$. This solid $AlCl_3 \cdot 6H_2O$ is thermally decomposed to produce alumina and to recover HCl for reuse.

Iverson and Leitch[4] conducted a series of experiments on alumina extraction by autoclave precipitation of basic sodium aluminum sulfate. Synthetic solutions containing Na_2SO_4, $Al_2(SO_4)_3$, H_2SO_4 and H_2O were used and virtually all of the alumina could be precipitated as natroalunite

[$NaAl_3(SO_4)_2(OH)_6$]. The optimum time and temperature for autoclaving were 20 to 30 minutes at 200°C. Upon heating, the natroalunite precipitate decomposed without melting to yield SO_3 and SO_2 gases and a solid composed of Na_2SO_4 plus gamma and alpha Al_2O_3; continued heating to 1200°C produced Na_2SO_4 and alpha Al_2O_3. Water leaching of this product removed the Na_2SO_4 and left a final residue of alpha Al_2O_3.

Scott[5] has described a process developed by Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia by which alumina can be recovered from its ores with a sulfuric acid process. The resulting solutions are hydrolyzed at temperatures around 200°C to obtain a product which is described as a basic aluminum sulfate closely related to the mineral alunite. Then calcination is carried out in the range of 900-1300°C, the temperature depending on the type of alumina required and the amount of tolerable residual sulfur.

Apparently, the extraction of aluminum from copper-leach solutions is an established fact, and the aluminum content of these solutions could be removed by several methods that have been studied in other contexts. The unknown factors to be considered and investigated include the pickup of new aluminum per cycle, the effect on the copper/leaching process of highly acidic solutions resulting from hydrolysis and the effect on copper leaching due to removing aluminum from the dump solutions to prevent its precipitation as a jarosite.

The U.S. Bureau of Mines has recently conducted some pioneering work on removal of values including alumina from copper tailing leach solutions; the program was completed in June 1970 and will be reported soon.

Kennecott has a pilot plant operating on leach solutions from an isolated copper dump to determine the rate of pickup of various materials.

Recovery of alumina is not the primary interest, but data on alumina will probably be obtained.

3. Conclusion. Although the recovery of alumina from copper leach solution may prove economic, this raw material does not represent a potentially large source of supply.

REFERENCES

1. Spedden, H. R., and Schellinger, A. K., U.S. Patent 3,436,177, April 1, 1969.
2. Spedden, H. R., and Schellinger, A. K., U.S. Patent 3,436,176, April 1, 1969.
3. George, D. R., et al, J. of Metals, vol 20, No. 9, (September 1968).
4. Iverson, H. G., and Leitch, H., Alumina Extraction by Autoclave Precipitation of Basic Sodium Aluminum Sulfate, U.S.B.M. R.I. 7162 (1968).
5. Scott, T. R., Extractive Metallurgy of Alumina, vol 1, Interscience Publishers, New York (1963).

H. Miscellaneous

1. Saprolite. Saprolite is soft-weathered rock in which nearly all the original minerals have been replaced by weathering products but the original textures and structures have been preserved. Large areas of aluminous saprolite are scattered throughout a belt in the Piedmont Region of southeastern United States, extending from southern Virginia, through the western Carolinas and northern Georgia, into northeastern Alabama. Saprolite also is associated with low-grade bauxite in Hawaii, Washington, and Oregon; and it occurs in other parts of the country.[1]

Saprolite has been investigated by industry as a possible source of alumina, but very little information on this rock has been published. In the

1950's, aluminum companies investigated large areas in the vicinity of Spartanburg, S. C., and Rutherfordton, N. C., and in 1970, a company investigated the possibilities of recovering gibbsite from saprolite in southern Virginia and northern North Carolina.[2] Twelve samples of saprolite from the vicinity of Shelby, N. C., and Gaffney, S. C., were analyzed in Geological Survey laboratories and ranged in alumina content from 25 to 36 percent.[1] Part of the alumina is in fine-grained gibbsite, but much of it is in aluminum silicate minerals.

Conclusion. Today, insufficient information is available to evaluate saprolite as a potential domestic source of alumina.

2. Aluminous Shales. Aluminous shales, as a possible source of aluminum, have been investigated by several state geological surveys and other agencies and, to a limited extent, by industry.[1,3] Also, they were used as a source of aluminum by Japan during World War II. Probably the most thorough effort to extract alumina from shale in the United States was by the North American Coal Corporation, which built a pilot plant at Powhatan Point, Ohio.[1] The shale treated in this plant was mainly roof stone above the Pittsburgh coal bed and contained 20 percent or more alumina. The pilot plant was unsuccessful and was dismantled in the early 1960's.

Resources of shale in the United States containing 20 to 22 percent alumina are inexhaustible, and rock of this grade occurs in several parts of the country. A few shales and similar fine-grained rocks that have been metamorphosed are considerably richer in alumina than 22 percent but, at present, insufficient information is available to evaluate these rocks as potential aluminum resources.

Conclusion. In the Panel's judgment, most aluminous shales are too low in alumina content to permit profitable extraction of aluminum; however, some shales eventually may be found to merit more consideration than is given here.

3. Alunite. Alunite is used now as a source of alumina in the Soviet Union and has been investigated as a possible source of aluminum in several countries. During World War II, it was also one of the raw materials investigated as an emergency source of aluminum in the United States and research on it was carried through the pilot-plant stage. However, this Panel did not consider alunite to be a source of aluminum with economic potential because no large pure deposits are known to exist in this country. Although the total alunite in the western United States may eventually be found to amount to hundreds of millions of tons, all known deposits occur in such form that large tonnage of uniform grade could not be mined. The beneficiation of disseminated alunite would be too costly to be competitive with other aluminous materials.

Conclusion. Alunite has little potential for being a major raw material of aluminum in this country because all known deposits are either small and scattered or have the mineral disseminated through volcanic rock. Alumina extracted from such material would not be competitive in price.

4. Coal Ash. Coal produced annually in the United States yields approximately 50 million tons of ash when burned. This estimate was made on the following basis. Yearly production of bituminous coal, lignite, and anthracite is now a little more than one-half billion tons (U.S. Bureau of Mines Mineral Yearbooks). Coal ash contents range from approximately one to thirty-three percent on a moisture-free basis. The average ash content of bituminous coal in the Ohio River Valley region, which includes most of the major producing states, is 9.5 percent.[4] The alumina content of ash in 373 samples from the entire country ranges from 8.0 to 41.6 percent. Most bituminous coal ash has 25 to 35 percent alumina and much of the ash from lignite has only 18 to 19 percent alumina.

Insofar as this Panel is aware, no nationwide studies have been made showing the locations of coal-ash accumulation centers, quantities and compositions of ash generated, and present uses. Obviously, the locations of coal-producing districts have only broad regional influences on its marketing and areas of consumption.

Conclusion. The quantities of ash generated at any one place are insufficient to be considered as a raw material of aluminum. Further, restrictive requirements on atmospheric pollution might further reduce the amount of ash generated at localities where aluminous raw material would be desired. The possibilities of using coal ash as a source of alumina also may be lessened by the following: (1) the wide range of alumina contents of ash make raw-material quantity control difficult or costly and (2) much coal ash has been heated to such high temperatures that the alumina present is in relatively insoluble compounds.

REFERENCES

1. Patterson, S. H., Bauxite Reserves and Potential Aluminum Resources of the World: U.S. Geological Survey Bulletin 1228, 1967, 176 pp.

2. Engineering and Mining Journal, "Gibbsite Corporation hopes new patent will allow gibbsite mining for aluminum in South," Eng. Mining Journal, 1970, vol 171, No. 2, p 110.

3. U.S. Bureau of Mines (staff), Potential Sources of Aluminum: U.S. Bureau of Mines Information Circular 8335, 1967, 148 pp.

4. Abernethy, R. F., Peterson, J. J. and Gibson, F. H., Major Ash Constituents of U.S. Coals: U.S. Bureau of Mines, Report of Investigations 7240, 1969, 9 pp.

V. OTHER PROCESSES

A. Electrolysis of Aluminum Chloride

1. General. The production of aluminum by the electrolysis of aluminum chloride has received the attention of a great many investigators. Indeed, the literature includes well over 600 references bearing directly or indirectly on the production of aluminum chloride, its properties, the properties of systems containing it, and its electrolysis to yield metal.

2. The Process. There have been a number of reasons for the interest shown in processes for aluminum via aluminum chloride:

a. Selective chlorination appeared to offer a technique for obtaining a "reduction grade" raw material from aluminiferrous ores not economically amenable to the Bayer process.

b. Low melting simple chloride baths containing $AlCl_3$, presented the possibility of electrodepositing aluminum at such low temperatures as to greatly alleviate the materials-of-construction problem that is so troublesome in the Hall cell.

c. The chloride electrolysis cell would use essentially permanent anodes, long a desideratum in aluminum production schemes. Cell designs exploiting permanent anodes could lead to economies in floor space and operating labor, because of the large ratios of cathode area to cell volume envisioned.

d. The inherent simplicity of feeding cells with $AlCl_3$ gas or liquid offered the possibility of eliminating much of the labor necessary for the control and operation of the Hall cell.

e. Power efficiencies greater than those possible with the Hall cell seemed attainable, due to two factors: (1) chloride baths generally have higher conductivities than the fluoride baths used in the Hall cell, and (2) compact chloride cells could be operated at relatively low current densities.

f. The costs of chloride bath components are generally less than those of fluoride bath components.

A preliminary economic analysis, based on a tentative design for a commercial bipolar cell, indicated promise for the production of aluminum by the electrolysis of $AlCl_3$. Among the more important assumptions made in the tentative cell design were:

(1) Horizontal pads, 2 inches thick, supported on graphite plates separated by alumina spacers.

(2) Graphite anodes.

(3) Current density: 1.3 amp/in.^{2}

(4) Cell voltage: 3.0 volts/electrode pair.

(5) Current efficiency: 70 percent.

(6) Cell life to exceed 3 years.

An experimental unit was built and operated to test the validity of the design assumptions.

3. Conclusions. The experimental cell was not a success. The electrolysis of aluminum chloride was concluded as unlikely to compete successfully with the Hall process. Of course, such a conclusion is tentative in the sense that future technological advances in materials of construction might permit a different set of assumptions.

Extreme difficulty was encountered in operation of the experimental unit, owing to formation of sludge. The sludge consisted of aluminum carbide and alumina. The great magnitude of the problem indicated that a proposed commercial cell would be inoperable.

Current efficiencies were found to be less than 60 percent. Although these low current efficiencies might have been caused by too shallow pad and sludge formation, the proposed design for a commercial cell apparently would not increase the efficiencies.

B. Other Aluminum Reduction Processes

1. General. New reduction technologies are being developed, including direct reduction processes, but none have proven economically attractive. The processes below have been considered within the last ten years by one or more of the aluminum companies.

2. Subhalide. The subhalide process was investigated by Alcan on a semicommercial scale. During the investigation of the process, Alcan covered salient features with patents obtained in many countries. Mechanical and corrosion problems have proven very difficult to overcome. At the time the pilot plant work was stopped, Alcan President N. V. Davis made the following statement:[1]

> "An intensive reappraisal of the economic potential of the direct reduction process has just been concluded. As a result, it has been decided that the probability of achieving adequate profitability within an acceptable number of years does not justify a continuation of the present rate of development or the heavy expenses involved in bringing the Arvida experimental production unit into operation."

In this process the bauxite or other alumina raw material is reduced in an electric-arc furnace with carbon at high temperature to form an impure aluminum-silicon-iron alloy. This material is reacted with aluminum trichloride vapor in an unpressurized reactor at 1,000° - 1,200°C. At the reaction temperature, the volatile aluminum monochloride forms and flows to a condenser, leaving impurities behind. In the condenser, a pool of molten aluminum is maintained at 700° - 800°C. An impeller is used to shower this molten aluminum through the incoming monochloride gas. The molten metal cools the gas, causing the initial reaction to reverse, condensing aluminim and forming aluminum trichloride, which is recycled.

Production of the alloy on a large scale was considered successful, but problems in the distillation step remain to be solved. If clay were used instead of bauxite, the energy and coke requirements would be approximately double the needs for bauxite for equal weights of aluminum in alloy.

Because of anorthosite's large lime content (about 11 percent), it is unlikely that anorthosite could be reduced to an aluminim alloy of any significant aluminum content. The high temperature required to form a CaC_2 slag in the reduction step would probably vaporize most of the aluminum. The large coke and energy requirements for reducing clay, as compared with the requirements for bauxite, are due chiefly to the large quantity of silica in the clay as compared with bauxite.

3. <u>Crude Alloy Production With Mercury Leaching</u>. A German process, that was used on a small scale during World War II to process scrap, has been investigated by Reynolds Metals.[2] In this process an aluminum-silicon alloy is made in an electric furnace. The alloy is leached with mercury, dissolving the aluminum and leaving silicon behind. Mercury is then evaporated leaving a pure aluminum residue and the mercury is recycled.

4. <u>Carbothermic and Nitride</u>. Two processes, carbothermic and a nitride, have been investigated by Société Pechiney. Unlike the previous two processes, the carbothermic process requires pure alumina as feed. In this process alumina and carbon are reacted in a furnace at 2,500°C forming aluminum carbide and some carbon and aluminum. The aluminum carbide is removed, heated, and decomposed and the aluminum metal is condensed. The nitride process

involves the thermal production of aluminum nitride and the subsequent condensation of aluminum from this vapor. Although both techniques have been investigated on the pilot-plant scale, it is believed that work has been suspended.

5. Hydrogen Reduction. Another method that has been considered is hydrogen reduction which requires high pressure of about 100 atmospheres.

6. Electrolysis in an Organic Medium. A different approach is the preparation of aluminum metal by electrolysis in an organic medium. Although a great many techniques have been considered, none have reached the industrial stage due to the cost of electrolytes, the structure of the deposits, and the complicated apparatus required for the processes.

7. Conclusion. To date, none of the new reduction technologies that have been developed, including direct reduction, have been attractive economically.

REFERENCES

1. Beizer, James, "Alcan Gives Up Direct Reduction Program," The Iron Age, September 28, 1967, p 154.

2. Light Metal Age, "Improving a German Process for Direct Reduction of Aluminum," vol 24, October 1966, p 9.

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APPENDIX A

OCCURRENCE OF THE DAWSONITIC-SODIUM MINERALS WITH THE OIL SHALES OF THE COLORADO-WYOMING-UTAH AREA

The most extensive deposits of dawsonite known at present are those in the northern half of Colorado's Piceance Creek Basin, where approximately 20 core holes have been drilled into the oil shale-sodium minerals strata. However, only a few of these 20 cores have been subjected to detailed mineralogical and chemical analyses. Even in these few cases, complicated mineral and analytical problems have been encountered.[1] As a result, much still remains to be learned about dawsonite, its occurrence, mineralogy, and its physical and chemical properties.

Probably dawsonite is also present in other basins within the region but, as yet, no deposits comparable in size to those in the Piceance Creek Basin have been found. For example, to date, reportedly more than 100 core holes have been drilled in the shallow trona beds associated with oil shale in the Green River Basin in Wyoming, but the existence of extensive deeper dawsonite deposits in this region is still unknown. In Utah, the existence of sodium minerals in the Green River Oil Shales of the Uinta Basin has been shown in a few core holes from the area. However, at present, the available data are far too limited to assume the presence of extensive dawsonite resources in that Basin.

In spite of these limitations on the data, preliminary surveys by the U.S. Department of the Interior[2] and others indicate that, in 150,000 acres of the sodium-minerals rich oil shales portion of the Piceance Creek Basin, there are an estimated 27 billion tons of dawsonite, equivalent to 9.5 billion tons of alumina.

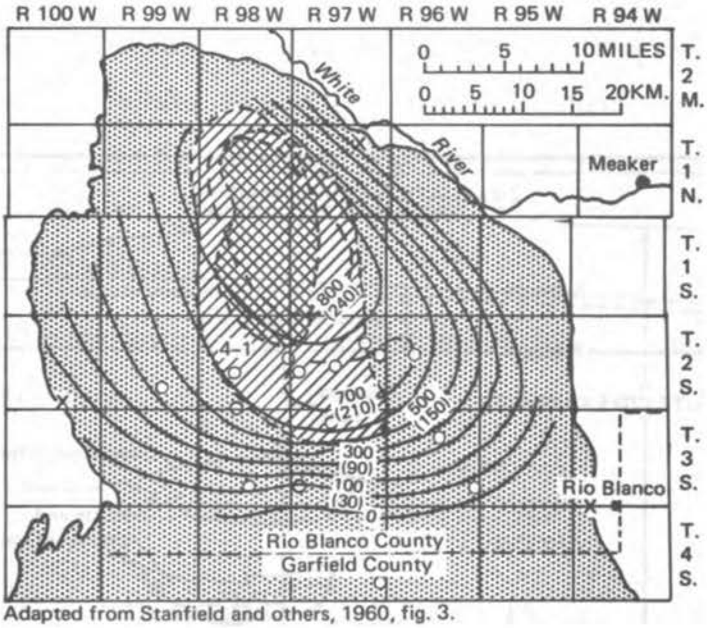
In addition, there is thought to be an estimated 30 billion tons of nahcolite. In only one square mile (640 acres) of the dawsonite-rich area, the potential alumina from the dawsonite itself is calculated to be 42 million tons. In addition there are estimated to be 130 million tons of nahcolite and 1 billion barrels of shale oil. The resources of dawsonitic oil shale in the Piceance Basin alone appear to be sufficient incentive to investigate dawsonite as a future domestic source of alumina. This is true whether additional large resources of this mineral are found subsequently in the Green River oil shale deposits of Wyoming and Utah, and in the Colorado Basin as well.

Piceance Creek Basin Dawsonite

Dawsonite and nahcolite in the Piceance Creek Basin of Colorado (Figure 10) are present in the lower half of the Parachute Creek Member of the oil shale-bearing Green River Formation. This Member is approximately 800 feet thick on the outer rim of the Basin, and nearly 2,000 feet thick near the center. The lower, sodium-rich zone of this Member is nearly 1,000 feet in thickness at the center of the saline deposit, extending in depth from 1,600 feet to 2,600 feet below surface in the central part of the Basin.

The stratigraphy and nature of these saline deposits have been described in two excellent papers: by Hite and Dyni[3] and by Smith and Milton,[4] from which the following information has been taken: The dawsonite, nahcolite, halite, etc., are intermixed with rich oil shale (typical value: 30-35 gallons per ton). Three nahcolite strata are present near the base of the saline zone (Figure 11), and two halite-bearing strata in the upper part of the zone.

The thickness of the dawsonite-bearing deposits (finely commingled with other sodium minerals in oil shale) ranges from zero at the Rio Blanco County line (southern edge of Basin) to nearly 700 feet near the center of the Basin. It



Adapted from Stanfield and others, 1960, fig. 3.

EXPLANATION

░ **Area of Green River Formation**

▨ **Area of nahcolite units 1, 2, and 3**

▧ **Area of halite deposition**

——— 500 (150) ———

Isopachs in feet and meters (approximate) drawn on thickness of dawsonite-bearing oil shale. Isopachs are based on bore-hole data from Smith and Milton (1966) supplemented by outcrop data by D. A. Brobst, U.S. Geological Survey. Control wells are shown by circles and surface sections by X's.

Figure 10. Distribution of Dawsonite, Nahcolite, and Halite in Piceance Creek Basin Oil Shales

Source: "Potential Resources of Dawsonite and Nahcolite in the Piceance Creek Basin, Northwestern Colorado," Colorado School of Mines Quarterly 62, No. 3. (1967)

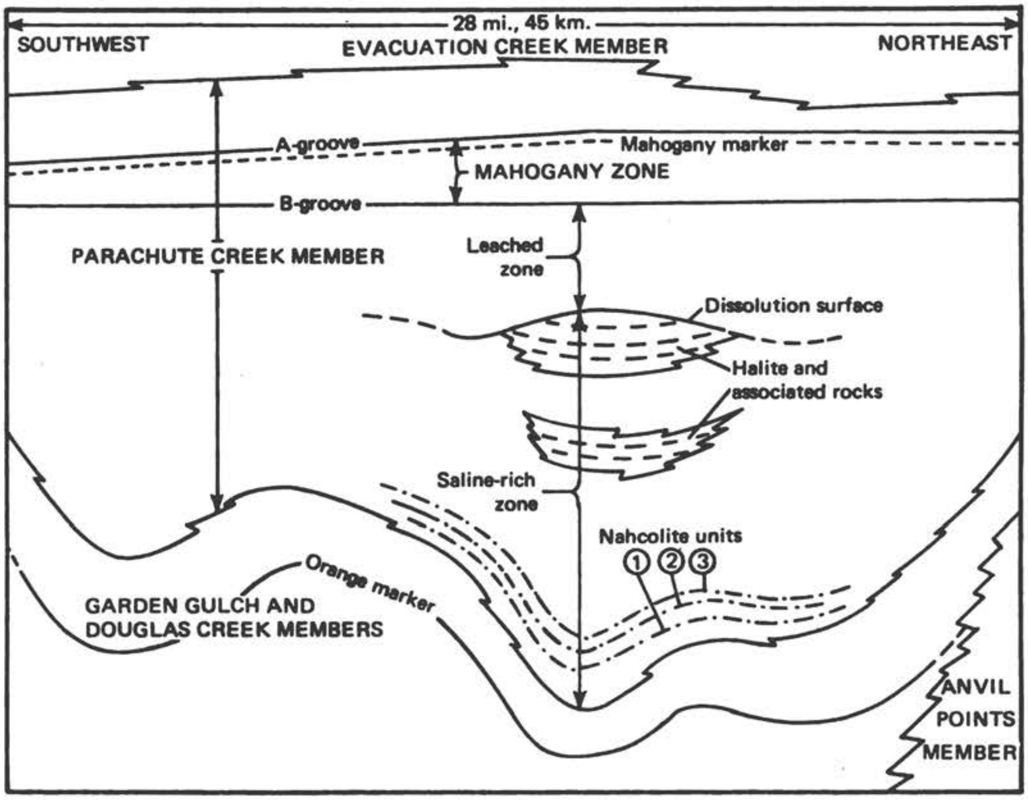


Figure 11. Stratigraphic Section (Southwest-Northwest) through Piceance Creek Basin Saline Zone

Note: Dawsonite occurs throughout saline zone and is particularly abundant in nahcolite units.

Source: "Potential Resources of Dawsonite and Nahcolite in the Piceance Creek Basin, Northwestern Colorado," Colorado School of Mines Quarterly 62, No. 3, (1967) thins to 300 feet on the northern and western edges, and to zero on the eastern side of the Basin. The top of the dawsonite zone in the Basin's center ranges from 900 to 1,800 feet below the surface. The dawsonite is associated, in various amounts, with quartz, albite ($NaAlSi_3O_8$), potash feldspar, dolomite, nahcolite, and illitic clay. The ratio of quartz to dawsonite is nearly constant at 2.5:1. Most of the clay occurs below 2,400 feet in depth and is rare above this horizon, where nahcolite is most common.

A "typical" composition of the dawsonite-bearing rock has been given by Nielsen,[5] as follows:

	Average Weight Percent*
Dawsonite	12
Nahcolite	20
Potash Feldspar	12
Dolomite	14
Calcite	3
Silica	24
Oil Shale Kerogen	15

*Pyrite is not shown, but may average 1 percent.

The percentages shown above are average values of representative thick sections. It is possible, by specifically selecting certain minable zones to obtain a dawsonite content anywhere from zero to as high as 20 percent. Similarly, nahcolite content can be varied from 0 to 90 percent and oil shale kerogen content from 10 to 30 percent.[5]

REFERENCES

1. Schmidt-Collerus, J. J., and Hollingshead, R. D., "Investigations Into the Nature of Dawsonite in the Green River Formation," Colorado School of Mines Quarterly <u>63</u>, No. 4, 143-167 (1968).

2. "Prospects for Oil Shale Development, Colorado, Utah, and Wyoming," U.S. Department of the Interior, May 1968.

3. Hite, R. J., and Dyni, J. R., "Potential Resources of Dawsonite and Nahcolite in the Piceance Creek Basin, Northwestern Colorado," Colorado School of Mines Quarterly, <u>62</u>, No. 3, 25-38 (1967).

4. Smith, J. W. and Milton, C., "Dawsonite in the Green River Formation of Colorado," Econ. Geology <u>61</u>, No. 6, 1029-42 (1966).

5. Nielsen, I., <u>Engineering Mining J.</u>, January 1969, p 57-60.

APPENDIX B

ECONOMICS OF RECOVERING ALUMINA FROM ANORTHOSITE

I. GENERAL

Cost estimates for recovering alumina from anorthosite using lime-soda sinter process were published in 1968.[3] These costs were based on the Marshall and Stevens Chemical Equipment Index of 240.0,which is equivalent to 1960 costs.

II. CAPITAL COSTS

The capital cost estimates are of the general type called "study estimates." This type of estimate, prepared from a flowsheet and a minimum of equipment data,can be expected to be within 30 percent of the actual cost. The fixed capital costs for the lime-soda sinter process for treating anorthosite are $75,714,000 for the dry grinding option and $69,601,500 for the wet grinding option for plants producing 1,000 tons of alumina per day.

III. OPERATING COSTS

The estimated operating costs are based on 350 days of operation per year allowing 15 days downtime for inspection, maintenance, and unscheduled interruptions. These costs are divided as direct, indirect, and fixed.

Direct costs include raw materials, utilities, labor, maintenance, and operating supplies. The raw materials costs, with the exception of anorthosite and limestone, do not include freight costs since the plant is assumed to be located near either the anorthosite mine or limestone quarry. Fixed costs are included in the cost of electric power since it is considered a purchased item.

On the other hand, fixed costs are not included in the cost of steam or water since these items are processed in the plant and their capital requirements are included in the plant capital cost. The direct labor cost is estimated on a basis of manning the plant with 4.5 men for each position that operates 24 hours per day, 7 days per week. Assignment of 4.5 men per operating position covers vacations and sick time. The costs of maintenance for steamplant, cooling towers, and electrical distribution equipment are included in the costs for steam, cooling water, and electricity, respectively.

Indirect costs are estimated at 50 percent of the direct labor and maintenance costs. The indirect costs include the expenses of payroll overhead, accounting, control laboratories, plant protection and safety, and administration. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of property taxes, insurance, and depreciation. The costs of taxes and insurance are estimated at 2 percent of the total plant cost per year. Depreciation is calculated using the straight-line method and a 20-year life.

Because large quantities of both limestone and anorthosite are needed for the process, the plant must be located in an area where both raw materials are available. A location next to the limestone quarry appears best since approximately twice as much limestone as anorthosite is used in the process. However, delivered costs for both anorthosite and limestone must be compared in order to select the plant location.

Assuming the cost of shipping the anorthosite is $1 per ton, and the cost of anorthosite at the mine is $1.50, and limestone at the quarry is $1 per ton, the estimated operating costs are $75.40 and $74.36 per ton of alumina for the dry and wet grinding options, respectively. These operating costs are itemized in Tables 6 and 7.

Because mining costs are different at various locations and because trucking costs will vary depending on the distance from the mine, the effect of delivered anorthosite and limestone costs on the operating cost are shown in a nomograph, Figure 12. To use this nomograph, connect the cost of anorthosite and the cost of limestone, left and right scales, with a straight-edge and read the total operating costs from the center scales, right for the dry grinding option and left for the wet grinding option.

TABLE 6. Estimated Annual Operating Cost for the Dry Grinding Option

	Annual Cost	Cost Per Ton Alumina
DIRECT COST:		
Raw Materials:		
Anorthosite at $2.50/ton	$ 4,256,900	$12.16
Limestone at $1.00/ton	3,082,500	8.81
Soda ash at $32.00/ton	952,000	2.72
Total	8,291,400	23.69
Utilities:		
Electric power at $.005/kw hr	1,345,800	3.85
Steam, 250-psig at $.50/M lb	873,600	2.50
Steam, recovered at $.10/M lb	323,400	0.92
Water, cooling at $.02 M Gal	66,200	0.19
Water, process at $.10/M Gal	142,700	0.41
Water, raw at $.01/M Gal	3,000	0.01
Natural gas at $.25/MM btu	3,540,200	10.11
Total	6,294,900	17.99
Direct Labor:		
Labor at $2.30/hour	1,813,100	5.18
Supervision, 15% of labor	272,000	0.78
Total	2,085,100	5.96
Plant maintenance, 5% of total section costs	2,078,300	5.94
Operating supplies, 15% of plant maintenance	311,700	0.89
TOTAL DIRECT COST	19,061,400	54.47
INDIRECT COST, 50% OF DIRECT LABOR AND MAINTENANCE	2,081,700	5.95
FIXED COST:		
Taxes and insurance, 2% of total plant cost	1,456,000	4.16
Depreciation, 5% of fixed capital cost	3,785,700	10.82
TOTAL OPERATING COST	$26,384,800	$75.40

Source: U.S. Bureau of Mines Report of Investigation 7068, 1968.

TABLE 7. Estimated Annual Operating Cost for the Wet Grinding Option

	Annual Cost	Cost Per Ton Alumina
DIRECT COST:		
Raw Materials:		
Anorthosite at $2.50/ton	$ 4,256,900	$12.16
Limestone at $1.00/ton	3,083,900	8.81
Soda ash at $32.00/ton	862,400	2.46
Total	8,203,200	23.43
Utilities:		
Electric power at $.005/kw hr	1,416,600	4.05
Steam, recovered at $.10/M lb	214,000	0.61
Water, cooling at $.02/M Gal	76,900	0.22
Water, process at $.10/M Gal	103,100	0.29
Water, raw at $.01/M Gal	3,100	0.01
Natural gas at $.25/MM btu	5,120,600	14.63
Total	6,934,300	19.81
Direct Labor:		
Labor at $2.30/hour	1,640,900	4.69
Supervision, 15% of labor	246,100	0.70
Total	1,887,000	5.39
Plant maintenance, 5% of total section costs	1,967,600	5.62
Operating supplies, 15% of plant maintenance	295,100	0.84
TOTAL DIRECT COST	19,287,200	55.09
INDIRECT COST, 50% OF DIRECT LABOR AND MAINTENANCE	1,927,300	5.51
FIXED COST:		
Taxes and insurance, 2% of total plant cost	1,338,500	3.82
Depreciation, 5% of fixed capital cost	3,480,100	9.94
TOTAL OPERATING COST	$26,033,100	$74.36

Source: U.S. Bureau of Mines Report of Investigation 7068, 1968.

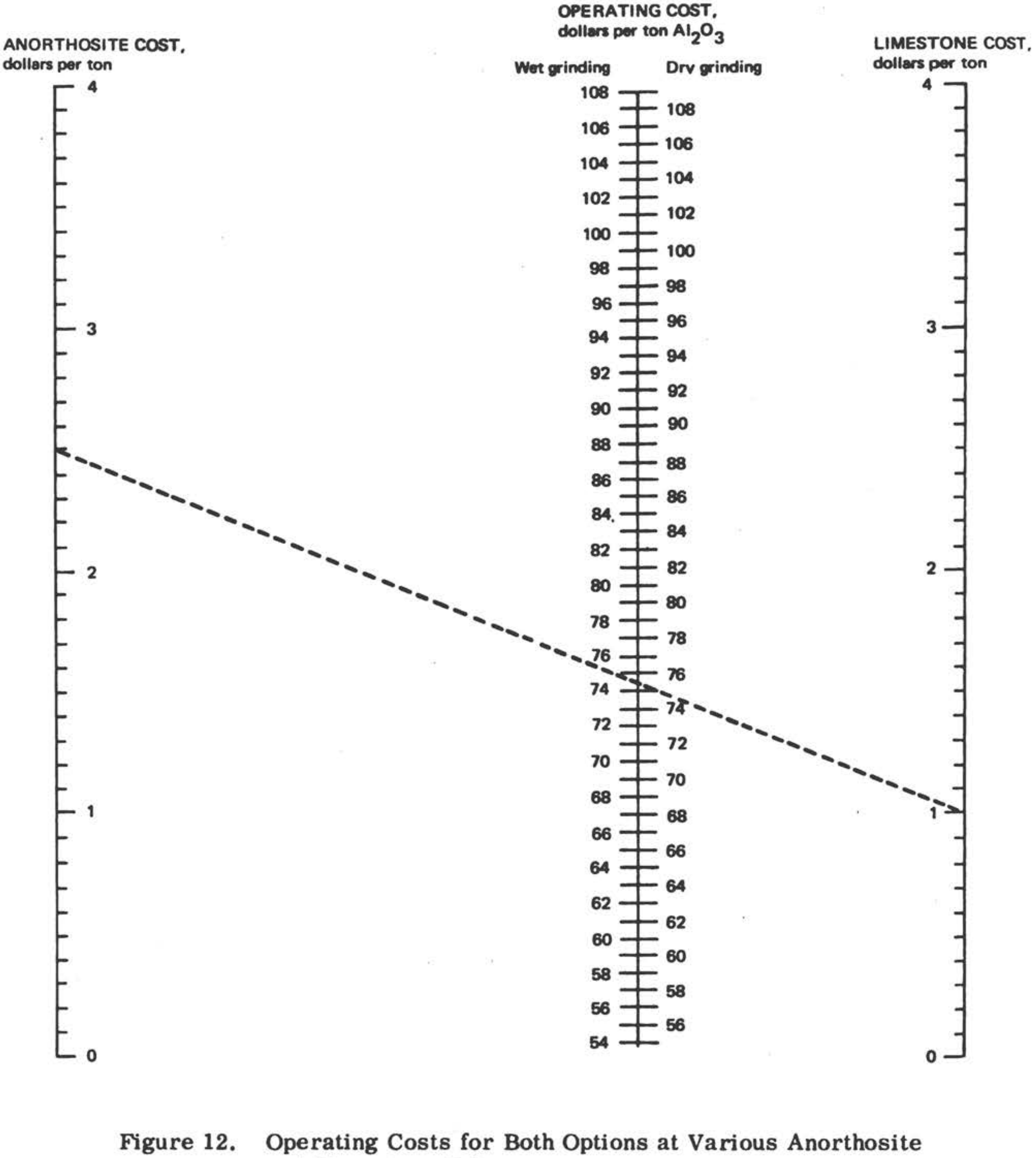


Figure 12. Operating Costs for Both Options at Various Anorthosite and Limestone Prices

APPENDIX C

RECOVERY OF ALUMINUM FROM SCRAP

I. MAJOR SOURCES OF SCRAP

Table 8 shows the total aluminum alloy content recovered from scrap or secondary materials by source as reported by the Bureau of Mines. The agency expands reported figures to an industry total to cover a number of unreporting firms.

Source data are available by type of scrap, i.e., new or plant scrap and old or obsolescent scrap. The quantities reported represent "merchant" scrap that only moves from one company to another. This includes all movements, whether on outright purchase, toll, conversion, or purchase and sale.

II. PROJECTED SCRAP BY MAJOR SOURCES

A. General

Projecting future scrap availability is a complex process involving expectations for domestic and imported primary supplies, withdrawals from stockpile, domestic and export, demand for aluminum, and destructive uses. The forecast below results from an independent study and the projections show minor deviations from figures published by the Bureau of Mines.

History indicates that new or plant scrap can be estimated by taking 18 percent of mill product and casting shipments lagged six months. Old scrap is generated from discarded finished aluminum products, e.g., aluminum cans, parts of automobiles, old airplanes, pots and pans. In 1969, can bodies and ends

TABLE 8. Aluminum Recovery From Secondary Materials By Source

Year	(Thousand Short Tons)		
	Total	From New Scrap	From Old Scrap
1960	438	343	95
1961	485	329	156
1962	582	415	167
1963	654	495	159
1964	707	545	162
1965	829	624	205
1966	887	700	187
1967	878	710	168
1968	997	791	206
1969	1,032	859	173
1970*	900	740	160

*Estimated by BDC; estimate by Reynolds Metals Company, Market Research Department is 900 thousand tons for 1970.

Source: BDC, Department of Commerce from reports by U.S. Bureau of Mines.

used an estimated 160,000 tons of which 103,000 tons went out in finished cans. For 1975, aluminum can production is expected to consume 412,000 tons, of which 250,000 tons will go out as finished cans and ends. Between 1969 and 1975, the increase in finished cans is expected to be 147,000 tons of which only a portion will be recovered. Those materials in steel and composite cans with aluminum ends are not likely to be recovered.

Table 9 shows estimated supply shipment and stock of aluminum in finished products since 1893 and illustrates the extent of aluminum growth.

Net aluminum stock is calculated by subtracting exports and recovered scrap from shipments and cumulating the totals for each decade. Conceptually, the aluminum in finished obsolescent items provide "old" scrap. The quantity herein is overstated because the subtractions should be gross weight of scrap rather than recovered weight and products that will never be recycled, such as powder and completely destroyed finished items. This overstatement of the available scrap causes an error of about five percent. The possible overstatement due to loss and other factors was not estimated.

At the end of 1969, there were over 50,000,000 tons of aluminum in finished items as a source for future recycling of secondary materials. By 1979, this figure should exceed 110 million tons.

Table 10 shows the projections of aluminum recovery from secondary materials for the years 1971 - 1980.

B. Categories of Scrap

One method of categorizing the various types of scrap available to the industry is as follows:

1. Segregated clean scrap, clips and solids.
2. Clean mixed low copper, clips and solids.
3. Segregated painted scrap, clips and sheets.

TABLE 9. Estimated Supply, Shipment and Stock of Finished Aluminum Products

Period	(THOUSAND SHORT TONS)						
	Total Supply	Primary Production	Recovered Secondary			Total Shipments	Net Aluminum Stock
			Total	New	Old		
Prior to 1900	8	5	1	1	X	8	7
1900 - 09	90	59	20	16	4	86	71
1910 - 19	569	405	96	73	23	546	512
1920 - 29	1,267	718	320	244	76	1,217	1,407
1930 - 39	1,459	961	380	290	90	1,401	2,368
1940 - 49	8,947	5,436	2,412	1,804	609	8,573	8,430
1950 - 59	19,757	13,617	3,612	2,765	847	17,368	22,011
1960 - 69	39,401	26,942	7,490	5,811	1,679	37,976	50,390
PROJECTED:							
1970 - 79	76,000	57,000	14,310	11,555	2,755	80,000	113,156

Source: Reynolds Metals Company, Market Research Department.

TABLE 10. Projected Aluminum Recovery From Secondary Materials By Source

Year	(Thousand Short Tons)		
	Total	From New Scrap	From Old Scrap
1971	1,050	875	175
1972	1,200	970	230
1973	1,275	1,025	250
1974	1,375	1,100	275
1975	1,500	1,200	300
1976	1,600	1,280	320
1977	1,700	1,360	340
1978	1,800	1,450	350
1979	1,910	1,550	360
1980	2,025	1,650	375

Source: Projected by Reynolds Metals Company Market Research Department.

4. Mixed scrap, clips, and solids.
5. Segregated borings and turnings.
6. Mixed borings and turnings.
7. Old castings and sheet.
8. High iron aluminum.

Generally, the value of scrap is based on the degree of segregation and contamination. The scrap in all the above categories is useful and is listed with the values in descending order.

Category 1 is used by the primary producers and the independent fabricators, such as the billet and sheet producers, and can be charged direct into the production furnaces. If its quality is sufficiently high, this scrap could represent up to 85 percent of the charge for some applications such as for independent extrusion billet producers. Some cost penalty may be incurred by substituting scrap for ingot as a result of increased handling costs. A 2,000 pound skid of briquetted or baled scrap could be handled for excess costs over ingot of not more than $0.001 per pound. By contrast, the excess costs for handling loose scrap might be $0.02 per pound. In addition, higher melt losses are to be expected from scrap as compared to ingot. This loss can vary from 2 to 20 percent or more, depending on metal thickness, coatings, and preparation of the scrap. An offsetting advantage of using scrap over ingot is that scrap, when properly segregated and identified, is already an alloy, reducing alloying costs.

Scrap in Category 2 is less desirable than Category 1 only because it cannot be specifically identified by alloy. When this material is charged into production furnaces, samples are taken to permit adjustment of the charge for the variation in alloy. This procedure increases the time for the standard furnace cycle and sometimes leads to off analysis ingot. Where analysis of the product is not closely restricted, as in some sheet alloy, this problem is minimized. Scrap of this category is also used in the production of secondary ingot. Since its use is limited by price and alloy, this grade has more utility in sheet plants when chemical analysis is not very critical.

Category 3 is also generally used in the production of sheet products. It is a low copper variety, either segregated or mixed, and is used principally in the manufacture of mill products by nonintegrated producers. This scrap should be processed through a reclamation furnace to control melt loss and air pollution. The favored types of reclamation furnaces are well type or salt bath furnaces to reduce melt loss. The salt bath is typically a mixture of sodium and potassium chloride with some fluoride addition. This scrap can be upgraded by processing through a reclamation furnace. After analysis, the melt from the reclamation furnace can successfully be transferred to production furnaces in molten metal form. Reclamation cost, if transferred molten, should not exceed $0.02 per pound more than charging clean segregated scrap with the same physical characteristics.

Categories 4 through 8 are the bread-and-butter items of the secondary ingot industry. Because of the variety of mixtures, they can be used best by the secondary ingot producers who have a wide variety of alloys with broad chemical specifications.

Most of the scrap generated in the marketplace can be and is used by the secondary ingot industry which produces a wide range of alloys. Problem elements in the secondary market are iron, manganese, and magnesium. Zinc was formerly troublesome but this problem has been minimized with the growing use of the 380 family of alloys that allow up to 3 percent zinc. The high magnesium alloys can be used, but the excess magnesium must be reduced by chlorine flux that is expensive especially in view of the additional melt losses and the problems of pollution.

The problem with manganese in secondary alloys is that only 0.2 - 0.3 percent Mn is allowed as in 380 alloys. Presently, there are no economical methods for removing the manganese; therefore, it must be diluted with other aluminum alloys low in manganese. Another problem comes from tramp iron picked up as ferrous attachments or free iron in various grades of scrap. Again, like manganese, iron cannot be removed and must be diluted for use. Scrap having the highest iron content usually finds it way into low grade deoxidizing products such as Grade IV shot or notch bar.

The melting of scrap through production furnaces or reclamation operations generates drosses that may contain widely varying amounts of metallics. Recovery of aluminum metal from dross is achieved regularly with the disposition of the metal governed by grade and quantity.

With proper care, much scrap may be upgraded. On the other hand, careless handling may downgrade otherwise quality metal with a consequent loss of value.

III. CONCLUSION

Secondary scrap (including new and old scrap) is an important but decreasing percentage (approximately 17 - 19 percent at present) of the necessary supply of aluminum.

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13. ABSTRACT

The most promising domestic sources of supply for alumina (other than commercial bauxite) were reviewed, basic approaches to the processing of clay were examined, and the most workable processes were appraised. An acid process for the treatment of clay appeared the most promising for the economic production of alumina from materials other than commercial bauxite. Available experimental and pilot plant data on most of the alkaline processes for producing alumina from clay indicated that these processes normally were not competitive with acid processes. The technical feasibility of producing near reduction-grade alumina by the hydrochloric acid extraction from clay has been demonstrated on a small scale. Relatively large and extensive pilot-plant testing appears necessary to assess the economies of scaled-up production and to evaluate other economic factors. The economic recovery of alumina from other sources does not appear promising at present.

National Research Council.
National Materials Advisory Board.
Processes for extracting
alumina from nonbauxite ores.