DAWSONITE: ITS GEOCHEMISTRY, THERMAL BEHAVIOR, AND EXTRACTION FROM GREEN RIVER OIL SHALE

John Ward Smith and Neil B. Young

ABSTRACT

Dawsonite \([\text{NaAl(OH)}_2\text{CO}_2]\), a rare mineral elsewhere, exists in huge amounts in Green River Formation oil shale of Colorado's Piceance Creek Basin. Occurring with the dawsonite is the aluminum trihydroxide, nordstrandite \([\text{Al(OH)}_3]\). Together these minerals represent a domestic resource of extractable alumina of over 6.5 billion tons. Analytical methods for determining dawsonite and nordstrandite in oil shale are described and evaluated. The geochemical conditions which produced these minerals in the oil shales are outlined. Thermal decomposition reactions of both minerals are described. With appropriate heat treatment dawsonite and nordstrandite both yield an alumina form readily and rapidly soluble in light base. A process based on extraction of alumina from properly prepared spent shale is compared with the Bayer process. Advantages in the extraction properties of spent shale may compensate adequately for the disadvantage of having to process ten times as much material to produce the same amount of alumina. Production techniques must be designed to exploit these advantages. Oil and soda ash are produced as coproducts with alumina. Electric energy generated by burning the shale oil is enough for aluminum metal production.

INTRODUCTION

Publications on dawsonite in Colorado oil shales have been appearing ever since 1966 when Smith and Milton showed that huge amounts of dawsonite existed in the Green River Formation oil shales of Colorado.

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and Nielsen (1969) emphasized the possibilities of this alumina resource in several presentations and papers. Factual information has been strongly exceeded by publicity and speculation, heavily colored by lack of understanding of the nature of oil shale and by an overpowering urge to produce alumina from oil shale by the Bayer process. However, a solid technical background exists. Published data are widely scattered, and each publication usually treats only a single facet of the multiple problems inherent in the mineral nature and in alumina (Al₂O₃) production from dawsonite-bearing oil shale. Incorporating data developed at the Laramie Energy Research Center, this report assembles and evaluates the information now available on: the oil shale minerals yielding extractable alumina; the nature of the deposit; the alumina resource in oil shale and the analytical methods developed to evaluate it; the geochemistry which created this unique deposit; the thermal behavior of the aluminum-bearing minerals and the oil shale containing them; and the alumina extraction this behavior permits. Finally, procedures for the extraction of alumina from oil shale are compared to the Bayer alumina extraction procedures, and the energy balance for producing metallic alumina is evaluated.

The United States consumed 6.5 million tons of aluminum metal in 1973 with less than 8 percent produced from alumina extracted from domestic ores (Mineral Industries Surveys 1974). Our bauxite and alumina imports for 1973 were valued at more than $400,000,000, and we are completely dependent on foreign alumina supplies. The U.S. Bureau of Mines has evaluated processes for producing alumina from nonbauxite domestic ores, and has continuously concluded that these processes are not economic. The production of alumina from Colorado oil shale as a coproduct with oil and sodium carbonates is an attractive prospect, spurring continued interest. Currently, however, development is blocked, because the federal government controls virtually all of the dawsonite resource and has refused to release any of its holdings to development.

MINERAL NATURE AND DISTRIBUTION

Extractable alumina arises from two minerals occurring together in oil shale. These minerals are dawsonite (NaAl(OH)₂CO₃) and nordstrandite (Al(OH)₃), and both minerals yield readily soluble alumina. Alumina also occurs in sodium and potassium feldspars and in illite clay in the dawsonite-bearing oil shale (Robb and Smith 1974), but like most forms of alumina in the world this is not readily soluble.

Before its discovery in oil shale, dawsonite was classed as an extremely rare mineral with only four known occurrences (Smith and Milton 1966). Dawsonite in the Green River Formation was noted first in 1959 by Milton and Eugster (1959), who reported its rare occurrence in vugs and fissures. In a 1963 study of changes in oil shale's organic matter with depth, Smith
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indicated that large amounts of dawsonite existed in oil shales deep in Colorado’s Green River Formation. Smith and Milton (1966) then collaborated to define the dawsonite occurrence, showing its presence in substantial amounts under a large area of the Piceance Creek Basin, stratigraphically located in the lower Parachute Creek Member in continuous sections to more than 700 feet thick. Subsequent study has shown two much less massive occurrences in Colorado oil shales, one just below the Mahogany Zone (Robb and Smith 1974) and the other in the Mahogany Zone (Smith and Robb 1973; Desborough and Pitman 1974), at specific locations in the Basin. However, the major dawsonite-bearing sequence is that initially described by Smith and Milton (1966). The geographic location and thickness of this major deposit is outlined in figure 1 (Beard, Tait and Smith 1974). Several subsequent publications show detail on the stratigraphic and geographic locations where dawsonite occurs in Colorado’s oil shale (Robb and Smith 1974; Beard, Tait and Smith 1974; Smith and

Figure 1.—Geographic location and thickness of Colorado’s dawsonite deposits (Beard and others 1974).
Dawsonite exists primarily as minute, discrete crystals disseminated in oil shale. Although Smith and Milton (1966) pictured several other modes of dawsonite occurrence, they carefully pointed out that most of it existed in tiny scattered crystals. Desborough and Pitman (1974) illustrated this in their microprobe study of oil shale minerals, saying "(Dawsonite) . . . is present as finely disseminated grains . . . most abundant in the (organic) rich layers."

Nordstrandite (Al(OH)_3) was recently identified by Milton and others (1975) as the crystal form of the other oil shale mineral yielding extractable alumina. In 1967 Smith and Johnson reported their thermal analysis detection of a mineral occurring with dawsonite. Decomposition of this mineral produced an endotherm on the differential thermal analysis (DTA) plot almost coincident with the primary dawsonite decomposition endotherm. Size relationship between the two peaks varied, and they could be separated by extraction with dilute acetic acid. All the dawsonite-bearing oil shales showed this extra DTA peak, while pure dawsonite did not.

Smith and Johnson (1967) concluded that the extra peak was produced by an unknown mineral, summarizing its observed characteristics as follows:

1. it dissolved in acid or alkali;
2. it contained aluminum but little or no sodium;
3. it was not detectable in oil shale by X-ray diffraction on powder samples;
4. it degraded thermally in two steps (as will be described later);
5. it coexisted in the shale with dawsonite.

They suggested it was a mineral form of Al(OH)_3, but could not identify it further. Schmidt-Collerus and Hollingshead (1968) subsequently detected this same pair of adjacent mineral decompositions by DTA on dawsonite-bearing oil shale. Although they managed some separation of the two minerals by sink-float techniques, they concluded that the two DTA peaks were produced by two forms of dawsonite. The Laramie Energy Research Center synthesized these two postulated dawsonite forms, finding that they behave identically in thermal analysis.

In developing and applying an analytical technique for determining dawsonite and the coincident nahcolite, Smith and Young (1969; 1970) consistently determined what they classed as "excess alumina." They defined this as acid-soluble alumina not associated with sodium. The proportion ranged from 0 to 31 percent, but an average of nearly 20 percent of the total extractable alumina was "excess alumina." The only mineral source for such alumina had to be an aluminum trihydroxide. Unable to identify it mineralogically, Smith and Young (1969; 1970) labelled this
mineral "gibbsite?". Goldberry and Loughnan (1970) then found nordstrandite with dawsonite in New South Wales, Australia. Milton and others (1975) identified nordstrandite in oil shales from the Piceance Creek Basin. Since the geochemistry forming the dawsonite creates the Al(OH)$_3$ form, nordstrandite, it appears probable that all of the Al(OH)$_3$ present with the dawsonite has this mineral form.

Nordstrandite occurs everywhere with dawsonite. Both thermal analysis (Smith and Johnson 1967) and chemical analysis (Smith and Young 1969; 1970) consistently demonstrate this. Consequently nordstrandite's distribution is similar to dawsonite's.

**ANALYTICAL METHODS**

Analysis of oil shale to determine its content of dawsonite and nordstrandite presents a formidable problem. Not only do these minerals share a common element (aluminum) but sodium-containing nahcolite (NaHCO$_3$) frequently occurs with them. Also always present in the oil shale are other minerals containing elements in common with dawsonite and nordstrandite: sodium feldspar, potassium feldspar, and illite clay. Still other Green River Formation minerals which might be present to furnish common elements are halite (NaCl) (Trudell and others 1970) and analcime (NaAlSi$_2$O$_6$·H$_2$O) (Smith and Young 1969). In addition dawsonite and nordstrandite are only a small part of any oil shale sample, rarely exceeding 15 weight percent.

The only analytical method capable of specifically determining both dawsonite and nordstrandite in oil shale was developed by Smith and Young (1969). They exploited the acid solubility of these minerals to separate them from the oil shale. Their method also determines nahcolite. In figure 2 we show a flow diagram of this analysis plan which separates nahcolite and then dawsonite and nordstrandite from the oil shale by successive leaches with water and hydrochloric acid. Analysis of the filtrates for sodium and aluminum yield values for quantities of the three minerals. Interference by halite is corrected where it occurs, and analcime does not occur significantly in the dawsonite-bearing oil shale. Two other successful methods for determining nahcolite have been described, but no other means is currently available for determining both of the extractable aluminum minerals in oil shale.

Intrumental methods investigated for these determinations include X-ray diffraction, thermal analysis, and infrared spectroscopy. Infrared spectroscopy did indicate the presence of Al(OH)$_3$ in oil shales (Huggins and others 1973) but did not provide satisfactory analytical resolution of the specific absorption bands. Thermal analysis which initially detected nordstrandite in oil shale gives responses suitable for analysis for both minerals. However, several specialized problems arise in the thermal
analysis of oil shale (Smith and Johnson 1967), and a procedure satisfactory for using this technique to determine these minerals has not yet appeared. Donald R. Johnson, thermal analysis specialist studying oil shales at the Laramie Energy Research Center, feels that combined differential thermal analysis and thermogravimetry (Smith and Johnson 1967) can measure both dawsonite and nordstrandite with accuracy better than the X-ray diffraction measurement of dawsonite.

X-ray diffraction initially detected dawsonite in oil shale and is extremely useful in defining dawsonite's occurrence profile (Robb and Smith 1974). Both the diffraction peak height and peak area respond quantitatively to dawsonite. Quantitative analysis by X-ray diffraction has many inherent perils, but dawsonite adds two more. First, dawsonite's primary diffraction response is sensitive to grinding. Extended or vigorous grinding sharply decreases the diffraction response (Huggins, Green and Turner 1973; Zen and Hammarstrom 1975). Because of this Zen and Hammarstrom (1975) concluded "that the X-ray diffraction method is not well adapted to the routine quantitative determination of dawsonite in oil shale.

Figure 2.—Chemical analysis flow diagram for dawsonite, nordstrandite, and nahcolite in Colorado oil shale (Smith and Young 1969).
of the Green River Formation.” Huggins and others (1973) didn’t quite agree, recommending the X-ray diffraction method to supplement the chemical analysis technique of Smith and Young (1969). The Laramie Energy Research Center attempted to avoid the grinding problem by minimizing and standardizing grinding time. This was successful enough to reveal the second difficulty Green River dawsonite presents to quantitative analysis by X-ray diffraction, namely, the degree of crystallinity of natural dawsonite appears to vary significantly. Both the peak height and the peak area of dawsonite’s primary reflection change with this variation, making quantity calibration uncertain. We agree with Zen and Hammarstrom (1975) that X-ray diffraction, while very useful semiquantitatively, is not well adapted to routine quantitative determination of dawsonite. In addition, it fails to measure nordstrandite.

Two additional techniques deserve mention. Neither offers analytical quantity determination of dawsonite and nordstrandite but each has value. The Oil Shale Corporation uses a base extraction on spent shale from oil yield assay to measure alumina available for extraction. Their procedure has not been published before this symposium (Haas and Atwood 1975), but within the limits of thermal behavior of dawsonite and nordstrandite, to be discussed later, and the possibility of base attack on clay and feldspars, their measurement of extractable alumina appears sound.

The second method involves use of already available data from oil yield assay to estimate nahcolite and dawsonite. During oil-yield assay, nahcolite, dawsonite, and nordstrandite also degrade, contributing water and carbon dioxide which is measured with the assay products. A procedure for estimating nahcolite and dawsonite from assay data was developed statistically (Smith, Beard and Wade 1972). The resulting nahcolite estimates are sufficiently accurate to permit stratigraphic plotting and correlation. The individual estimates for dawsonite are less accurate, offering only a generalized average. However, if the individual dawsonite estimates are pooled by calculating a total or average dawsonite content for a stratigraphic section, accuracy of the estimated average is much higher. The values estimated too high or too low tend to compensate each other. The resulting estimates of average dawsonite content values for stratigraphic sections lie within ± 10 percent of the actual mineral content. Nordstrandite values were not incorporated in development of these estimates because of statistical difficulties, but water arising from nordstrandite will tend to raise the dawsonite estimates. Consequently, the resulting estimate of total extractable alumina in a stratigraphic section is a good approximation.

ALUMINA RESOURCE

Measuring the dawsonite-nordstrandite resource will be a massive job requiring accurate analysis of many samples. Although some accurate
analytical data is available (Smith and Young 1969; 1970), the job is barely begun. Consequently, an estimate of the resource based on the extensive assay data available cross the deposit furnishes the best current evaluation. Beard and others (1974), prepared such an estimate, the first based on deposit-wide analytical data. The thickness contours for the dawsonite-bearing interval and the limit of the significant dawsonite resource given in figure 1 came from that paper. The thickness decreases away from the center of deposition. So does the relative amount of dawsonite. The dawsonite reserves in the Piceance Creek Basin (Beard and others 1974) are mapped in figure 3.

Total alumina resource estimated from oil-yield assay data was 6.5 billion tons (Beard and others 1974). This estimate represents enough alumina to supply United States demand for hundreds of years, demonstrating the significance of this huge domestic resource.

![Figure 3](image-url)
GEOCHEMISTRY

The dawsonite-bearing oil shale deposit of Colorado is unique. No similar sedimentary deposit is known. Even the Green River Formation oil shales in Wyoming and Utah contain no dawsonite, although they are similar to the Colorado oil shale in most respects. Several features combine to emphasize the unusual nature of the deposit: (1) The occurrence of naturally formed dawsonite in huge quantities while this mineral is rare elsewhere; (2) its coexistence with nordstrandite, a combination known in only one other place (Goldberry and Leughnan 1970); (3) the presence of massive amounts of natural sodium bicarbonate (nahcolite) in the dawsonite-bearing oil shales while other natural nahcolite occurrences are minor; and (4) the incorporation of this remarkable group of minerals in oil shale with organic matter rich in hydrogen; and (5) a mineral assemblage that is predominantly authigenic (Smith 1974).

In his discussion of the chemistry of oil shale deposition in Colorado, Smith (1974) described conditions which led to the formation of dawsonite and nordstrandite. Oil shale genesis in the Green River Formation is shown to require a stratified lake kept permanently separated by the buildup of sodium carbonate in the bottom layer. The sodium carbonate accumulation in the bottom layer raised the water's pH to the level that the incoming fine particles of aluminosilicates largely dissolved and aluminate ion (AlO$_2^-$) collected in solution. When organic matter from the lake's upper layer reached lake bottom, it trapped some sodium carbonate water containing aluminate ion. As CO$_2$ evolved from the organic matter, the pH of the trapped water was lowered from above 11 to about 9. This condition precipitated dawsonite. Bader and Esch (1944) used almost identical conditions to synthesize dawsonite, pointing out that dawsonite was obtained only when the initial sodium carbonate to aluminate ratio was higher than 15 to 1. This condition was naturally met in the sediment (Smith 1974).

Two interrelated events accompanied dawsonite formation. Both were generated by the CO$_2$ supply arising from the organic matter. As the pH of the water decreased, sodium bicarbonate formed from the sodium carbonate solution as indicated in the following equation:

\[ \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{NaHCO}_3. \]  \hspace{1cm} (1)

Smith (1974) explains how this triggered nahcolite crystallization. As the pH of the interstitial water decreased, aluminate ion precipitated as aluminum trihydroxide as in the following equation:

\[ \text{AlO}_2^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3. \]  \hspace{1cm} (2)

Formed in this manner the Al(OH)$_3$ either precipitated as in Papée, Tertian and Biais (1958) or altered to nordstrandite (Schoen and Rober-
These two products came to equilibrium with dawsonite according to the following equation:

$$\text{NaAl(OH)}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 + \text{NaHCO}_3$$  \hspace{1cm} (3)

This equilibrium explains the persistent occurrence of nordstrandite with dawsonite. Because dawsonite predominates in the oil shales (Smith and Young 1969), the equilibrium of the equation was toward the left, explaining the difficulty of locating nordstrandite without dawsonite in Colorado oil shale.

**THERMAL BEHAVIOR**

The dawsonite and nordstrandite in oil shale yield readily extractable alumina if they receive appropriate thermal treatment. Consequently, knowledge of their thermal behavior is vital. Because these minerals exist as matrix minerals in the oil shale, the thermal behavior of the balance of the rock significantly influences alumina extractability. The organic matter and the nahcolite in dawsonite-bearing oil shale affect alumina extractability most, so their thermal behavior will be described with that of dawsonite and nordstrandite.

Dawsonite decomposes around 350°C according to the following equation (Smith 1972):

$$2 \text{NaAl(OH)}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 + 2 \text{H}_2\text{O} + \text{CO}_2.$$  \hspace{1cm} (4)

Simultaneous DTA and weight loss curves for this decomposition are shown in figure 4. The dawsonite sample demonstrating this decomposition pattern was natural African dawsonite (Hay 1963), a well-crystallized specimen, containing no nordstrandite. The weight loss approximates that predicted in equation (4). Equation (4) is not quite accurate, however, because the alumina form appears to retain a small amount of water. The only reflections we detected from the product by X-ray diffraction over the interval from 370°C to nearly 700°C were faint reflections of sodium carbonate. The presence of sodium carbonate in this decomposition residue was verified by Huggins and Green (1973) using infrared absorption. The balance of the residue showed no significant crystallinity. Of the possible products only the chi-alumina form of Al_2O_3 produces X-ray diffraction patterns sufficiently diffuse to be difficult to detect (Tertian and Papée 1958). Brindley and Choe (1961) point out that chi alumina gradually loses water once it forms. The gradual water loss detected by Huggins and Green (1973) from artificial dawsonite supports the chi-alumina form. Because dawsonite has an aluminum-trihydroxide-type structure, symbolized by writing its formula in this manner,
and because it largely exists in fine particles in the oil shale, it probably produces chi alumina, as fine-grained gibbsite does (Brindley and Choe 1961). Tertian and Papée (1958) point out that the chi alumina produced from fine particles of gibbsite is highly susceptible to rehydration, generating its elevated solubility after its escape from the dawsonite structure.

The name “chi alumina” may not be completely accurate for the alumina form resulting from dawsonite degradation. Detailed study of dawsonite may eventually define the nature of the alumina product, but this is a horribly difficult task to attempt on a natural material. In the

**Figure 4.**—Simultaneous DTA and TG on nordstrandite-free natural dawsonite (Smith 1972).
meantime, many of the properties outlined for the dawsonite product resemble those of chi alumina prepared from fine-grained gibbsite (Tertian and Papée 1958), so we will call it "chi alumina."

As the dawsonite residue is heated to higher temperatures (fig. 4), the water from the chi alumina is gradually lost. In addition substantial amounts of CO₂ evolve as the product sodium carbonate attacks the alumina in a solid-state reaction. At about 700°C a burst of CO₂ is lost, and a crystallization exotherm appears. At this point crystalline sodium aluninate (NaAlO₂) is detectable in the product by X-ray diffraction (Smith 1972; Huggins and Green 1973). Production of sodium aluninate is not quantitative because of mobility problems inherent in solid-state reactions. In oil shale, this solid-state reaction would involve even less of the dawsonite products.

The thermal decompositions of nordstrandite and gibbsite are virtually identical (Milton 1975). Fine-grained gibbsite decomposes to chi alumina (Brindley and Choe 1961). Coarser-grained gibbsite can decompose by a different route, first losing part of its water to form the boehmite structure near 300°C, then losing the balance of its water near 500°C to form gamma alumina (Lodding 1969). In their paper describing their initial detection of nordstrandite, Smith and Johnson (1967) reported an unexplained DTA peak at about 500°C which appeared to be associated with the nordstrandite peak near 300°C. Pure dawsonite showed no such peak. This indicates that part of the nordstrandite has crystals sufficiently large to become gamma alumina. The amount of nordstrandite which will form gamma alumina varies with heating rate and reaction atmosphere as well as crystal size. Gamma alumina is much less soluble than chi alumina (Tertian and Papée 1958); consequently, this part of the nordstrandite alumina can't be easily recovered from spent shale.

Oil shale is normally a nonwettable, nonporous rock. However, after oil shale is heated to produce oil, spent shale wets readily with water and is full of holes arising from the virtual disappearance of the organic matter. Volume percent of organic matter in the oil shale rock can be estimated from oil yield using equations developed by Smith (1969). Shale yielding 30 gallons of oil per ton contains organic matter occupying 35 volume percent of the rock. The organic matter is finely distributed throughout the oil shale and is the largest component by volume (Smith 1969). When the organic matter in the rock decomposes under normal retorting procedures, about 80 weight percent of it is driven off as oil, water, and non-condensable gas (Smith 1962). This leaves behind a high-carbon coke which has a density well above 2 instead of that near 1 of the original organic matter. This coke occupies only about 10 percent of the volume the organic material originally occupied, so about 90 percent of the original organic volume is now void space. This is true until the shale becomes rich enough ( ~ 40 gpt) to collapse. After retorting, nearly one-third (31.5
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percent) the volume of 30 gallon per ton oil shale is pore space—interconnected, accessible, and water wettable. This porosity throughout the retorted shale provides access to the dawsonite and nordstrandite products.

Nahcolite in oil shale decomposes at low temperature (<130°C) as follows:

\[ 2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2. \]  \hspace{1cm} (5)

The nahcolite crystals don’t change in size or shape during this reaction, but they lose nearly 37 percent of their weight. The resulting soda-ash pseudomorph is extremely porous but sturdy. This material is more readily dissolved than nahcolite, and water will contain much more soda ash in solution than nahcolite.

The sodium carbonate generated from dawsonite and from nahcolite by heating has one detrimental effect if temperatures above 600°C are reached. It reacts with the other oil shale minerals, serving as a flux to form glass. Because the alumina and the sodium carbonate from dawsonite are close together in the oil shale, the glass formation tends to prevent alumina extraction. Coupled with the decrease in readily dissolved alumina accompanying the loss of water at higher temperatures, this glass formation makes temperature control during retorting vital to alumina extraction from spent oil shale.

EXTRACTION

Obtaining aluminum in solution is the object of any extraction procedure. If this can be achieved, economic judgments can begin. Alumina in dawsonite and nordstrandite can be dissolved to some degree by either acid or base from either the untreated shale or the shale residue after heat treatment, so each possibility should be considered.

Acid treatment will extract the nordstrandite and dawsonite from raw oil shale as shown by the success of the analysis method based on acid extraction (Smith and Young 1969). Base extraction will also separate part of the alumina, but this is less efficient because of dawsonite’s slow and limited base solubility.

Acid extraction of alumina from the raw shale presents some relatively expensive processing problems. The tough shale must be ground very fine, and because fine-ground shale is not water wettable, wetting agents are required for acid treatment. Because dawsonite is the least soluble in acid of the oil shale carbonates, alumina extraction with acid requires extracting all the carbonates in the ore. Acid is generally expensive, recovery of alumina from the calcium-, iron-, and magnesium-charged solution may be difficult, and for most acids regeneration is probably uneconomic. Suggestions for decreasing the cost of acid extraction of raw shale include treatment with CO₂ and water (carbonic acid) or with sulfurous acid.
obtained by solution of $\text{SO}_2$. The $\text{CO}_2$ in water is an inexpensive acid source, but it extracts dawsonite inefficiently. Sulfurous acid extraction (Peters and others 1962) may be feasible for recovering alumina from analcime in huge tuff beds like those occurring along the northern end of the Piceance Creek Basin, but is not strong enough to extract dawsonite. While strong acid extraction makes a good analytical procedure, it probably can't be an economic production method.

Base extraction of alumina from spent shale, the residue remaining after retorting for oil production, appears the best procedure. Acid extraction will also dissolve the alumina from spent shale, but its carbonate destruction and acid consumption problems still exist. Crushing and wettability problems are removed, but these are also simplified for base extraction. The spent shale is oil-free, porous, and water wettable. Its void space provides solvent access for alumina extraction. Each ore horizon will probably have an optimum particle size for extraction and separation. If size reduction is necessary, the spent shale crushes much more easily than raw oil shale.

The base extraction procedure used on spent shale should not be the Bayer process, now preparing virtually all the alumina consumed in this country. Its treatment is expensive, unnecessarily violent, and generally unsuited for extracting alumina from spent shale.

In the spent shale most of the alumina arising from dawsonite and nordstrandite is present in one form, chi alumina. It is much more easily dissolved in base than the gamma alumina (or boehmite at lower temperatures) arising from the balance of the nordstrandite. The amount of gamma alumina formed will vary with retorting conditions, but in any case base extraction will not recover all of the acid-extractable alumina found in the original shale.

Light base will extract the chi alumina from spent shale quite efficiently. In table 1 we illustrate the $\text{Al}_2\text{O}_3$ extracted by 0.5 M $\text{Na}_2\text{CO}_3$ from samples of nahcolite-free oil shale heated under nitrogen at temperatures of 450° and 600° for 30, 60, 90, and 120 minutes. The $-100$ mesh residue was extracted hot with stirring. Extraction time was 3 minutes, and longer times recovered no significant additional amounts of alumina. Shorter extraction times were not tested. Before heating, the specimen yielded 6.49 weight percent acid-extractable $\text{Al}_2\text{O}_3$, 5.15 percent in dawsonite and 1.34 percent in nordstrandite. About 94 percent of the acid-extractable $\text{Al}_2\text{O}_3$ was recovered at 450°C with heating times of 30 and 60 minutes. The high-carbon coke remaining on the shale did not interfere with the extraction.

Two factors which decrease alumina extractability are indicated in table 1. Significantly less alumina was available from the shale heated 600°C, and longer heating residence times appear to decrease the amount of extractable alumina. Similar decreases in alumina availability were
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Table 1.—Alumina extracted by 0.5 M Na₂CO₃ from oil shale heated at 450°C or 600°C in a nitrogen atmosphere

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<th>Shale heating time, min.</th>
<th>Alumina recovered wt pct raw shale*</th>
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<td>30</td>
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<td>60</td>
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<td>90</td>
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<td>120</td>
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*Extraction time 3 minutes.

noted when the samples were heated in air. At a temperature controlled to 450°C under air for 60 minutes, this same sample yielded only 5.4 weight percent Al₂O₃ to base extraction and a 600°C sample only 4.95 percent. Air over the sample undoubtedly burned part of the shale's organic matter, heating the sample hotter than the controlled temperature.

These solubility reductions stemmed from the two effects mentioned earlier, glass formation and the loss of water from the chi alumina. Heating to higher temperatures under nitrogen gradually reduced the amount of available alumina, indicating the gradual loss of water. Apparently the glass formation had used up the available sodium carbonate by 600°C. To test this, shale samples intimately mixed with NaHCO₃ (analogous to crushed nahcolite) were heated. This treatment at 650°C reduced the extractable alumina to only 10 percent although more than 80 percent had been available after heating the nahcolite-free sample at this temperature. Apparently limiting the temperature to no more than 550°C is essential to prevent glass formation. Elimination of nahcolite from the sample can help, but Na₂CO₃ from the dawsonite will always be present. The loss of water from chi alumina can be minimized by short residence times and use of a limited temperature range. Oil evolution from the raw shale can be completed quickly at about 450°C, the most suitable temperature neighborhood for heating oil shale for both oil and alumina production.

Dissolving chi alumina consumes base. The solution equation with sodium carbonate might be represented as follows:

\[ \text{A}_2\text{O}_3 + 2 \text{CO}_3^- + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- + 2 \text{AlO}_2^- . \]  
(6)

Production of the bicarbonate ion from the carbonate ion shows that one mole of hydroxyl ion was used up in dissolving one mole of aluminum. This equivalent reaction is

\[ \text{A}_2\text{O}_3 + 2 (\text{OH})^- \rightarrow 2 \text{AlO}_2^- + \text{H}_2\text{O} . \]  
(7)
The amount of aluminate ion which can be retained in solution depends on the amount of hydroxyl ion (pOH or the equivalent pH) in the solution (Pourbaix 1966). If the available base is consumed, the pH drops and solution of chi alumina will stop. This explains why water-leaching the retorted shale will not extract all of the available alumina. When dawsonite decomposes [eq. (4)], only one mole of carbonate is produced for two moles of aluminum in alumina. This is only half the base required [eq. (6)] to dissolve the alumina. In addition the nordstrandite product will require base to dissolve. If sodium aluminate were produced when dawsonite decomposes instead of the intimate sodium carbonate-chi alumina mixture indicated in equation (4), it would dissolve with little base consumption. Water extraction would then recover all of the dawsonitic alumina.

Enough base must be present in excess to maintain the aluminate ion in solution. If too much is consumed, the hydrolysis reaction

\[ 2 \text{ALO}_2^- + 4 \text{H}_2\text{O} \rightarrow 2 \text{Al(OH)}_3^- + 2 \text{OH}^- \]  

(8)

will buffer the solution. The reaction in equation (8) will limit alumina loss but the leach solution will dissolve no more alumina.

The other oil shale minerals are also exposed to light base when alumina is extracted from spent shale. The minerals include quartz, soda feldspar, potash feldspar, illite, iron-bearing dolomite, and pyrite (Robb and Smith 1974). These occur ubiquitously with dawsonite. All occur as very small particles and are usually well crystallized. Calcite will appear sporadically as will the siderite-magnesite cocrystal labeled “ferroan” (Young and others 1975). When oil shale is heated to 450°C in the inert atmosphere necessary for alumina recovery, quartz, the feldspars, illite, and calcite remain unaltered. Ferroan and dolomite will lose some CO₂ depending on residence time and CO₂ pressure in the retort. Extraction with soda ash will largely prevent solution of the carbonates and the residual oxides. Pyrite will become ferrous sulfide in the spent shale and will resist solution, although a small amount of soluble sulfide may appear because of H₂S attack on carbonates during retorting.

Only silica solution seems a possible problem. The tiny silicate particles present a huge contact surface but they are well crystallized and resist solution. Tests on silica solution at LERC indicate that relatively little can be dissolved. The small amounts will not interfere until aluminum trihydroxide is prepared for metal extraction. Here even tiny amounts are objectionable, so extraction conditions should be optimized to extract alumina and leave silica behind. Extracting with just enough base to dissolve the alumina and keep it in solution seems the best way to accomplish this. While this is easily done in a laboratory, commercial production will require continuous multiple extractions to raise the aluminate ion levels in the extract. Maintaining the most suitable base balance in such equipment may be a problem. The technique of successive base additions
described by MacMillan and Jackson (1972) coupled with the countercurrent decanter extractors described by Weichman (1974) seems to offer an attractive approach. If it can be accomplished, a deisilication step in a production process should be unnecessary.

Analcime occurs peripheral to the major dawsonite deposits. Production of alumina from areas where analcime occurs should be avoided, because analcime yields silica readily dissolved by base extraction.

The base extraction of spent shale seems the most probable route to alumina production from oil shale. This procedure is the basis of three workable patents for such alumina production (MacMillan and Jackson 1972; Hall and Haas 1970; Van Nordstrand 1968). All three use both sodium carbonate and sodium hydroxide in their extraction processes. These are equivalent in aluminum extraction, but sodium hydroxide is more useful than soda ash for pH control. Soda ash can be readily obtained as a by-product, and sodium hydroxide can be readily manufactured from it using heated limestone or perhaps the dolomite remaining in the shale after extraction.

To summarize the optimum procedures for extracting alumina from oil shale, the raw shale should first be heated to drive out the organic matter and decompose the nordstrandite and dawsonite. Atmosphere over the shale should be inert or at least not oxidizing in order to achieve temperature control of the retorting step. The shale should be heated between 450°C to no more than 550°C for only as long as is necessary to evolve the organic matter as oil. Burning the residual carbon coke is neither necessary nor desirable. The resulting spent shale is porous, permeable, wettable, and easily crushed. Crushing should be limited to that necessary to facilitate fast and efficient extraction but permit easy separation of the spent shale residue. The extraction should be rapid and continuous, and it should minimize shale exposure to strong base. Control of the amount of nahcolite entering the retorting process will help prevent glass formation and will also help the solvent recovery processes. The recovery of alumina from sodium aluminate solutions will probably involve precipitation of Al(OH)₃ with CO₂. This works well, and the procedures are known. Sodium concentration in the aluminum-bearing liquor must be kept low enough to prevent dawsonite formation during Al(OH)₃ precipitation.

COMPARISON WITH BAYER PROCESS

To compete with the long established Bayer process, still in use more than 80 years after issuance of its primary patent (Bayer 1894), a new process applied to a new ore must have technologic and economic advantages. Extracting alumina from oil shale seems to have such advantages. The primary advantage is that Colorado's dawsonite-bearing oil shale is
a huge domestic resource, irrefutably an asset.

The Bayer process requires ores high in alumina (~ 50 percent Al₂O₃) and low in silica (usually < 4 percent SiO₂) (Reese 1955). On this basis the oil shale is not a resource, so we need to evaluate what actually is available. In figure 5 we show the oil yield in gallons/ton and the dawsonite-nordstrandite alumina in weight percent of spent shale in a 277-foot interval selected from Bureau of Mines Colorado Corehole No. 2 (Smith and Young 1969). The corehole was drilled in sec 14, T 1 S, R 99 W, Rio Blanco County, Colorado. The interval selected for evaluation occurs at

Figure 5.—Oil yield and extractable alumina in spent shale from Colorado corehole number 2 interval, 1903 to 2180 feet (Smith and Young 1970).
the bottom of the leached zone. To avoid the complication of small amounts of nahcolite in the section, the values are calculated nahcolite-free. Average oil yield for the 277-foot section is 32.4 gallons per ton, and average alumina from dawsonite and nordstrandite in the spent shale is 4.97 weight percent. A plant processing about 30,000 tons of raw shale per day of this section could yield about 1,000 tons of alumina per day at 90 percent recovery. Preparing the shale for alumina extraction would produce 23,000 barrels of oil, and associated nahcolite plus dawsonite will produce soda ash. The required development of coproducts with the alumina is a significant asset to alumina production from oil shale.

Technologies of the Bayer process and the oil shale extraction contrast sharply, and several processing advantages to the oil shale extraction may compensate for the relatively small amount of alumina available per ton of spent shale. For equal alumina production, processing spent shale requires handling 10 times as much 5 weight percent \( \text{Al}_2\text{O}_3 \) material as does 50 weight percent bauxite. To point out advantages in spent shale extraction this process must be compared with the Bayer process (Bayer 1894). Unfortunately, in the United States the Bayer process is proprietary, and we couldn't find a review on it prepared since 1955 (Reese 1955). In 1966 Peters and others outlined the Bayer process as part of their cost study on alumina production. They point out that although the original process has been modified, particularly to adapt it to different ores, it is still basically the original Bayer process.

The Bayer process is shown in figure 6 (Peters and others 1966). The major contrasts between the two processes lie in the pressure digestion, clarification, and precipitation steps. Specific differences between the two processes will be itemized and evaluated.

**Pressure Digestion**

**Bayer**

Ore ground to \(-20\) mesh is digested at high pressure (commonly 200+ psig) and high temperature (to 400°F) in strong base (4 to 12 N) for periods of time ranging from 30 minutes to overnight (Reese 1955; Peters, Johnson and Kirby 1966).

**Oil Shale**

After inert atmosphere retorting to produce oil, alumina is dissolved from spent shale quickly and continuously in light base (\(~1\)N).

**Comparison**

The Bayer process is actually a batch process while oil shale retorting and extraction is a continuous process. The Bayer process is violent and
requires expensive specialized equipment for the extraction, including pressure and temperature control apparatus. It dissolves silica which precipitates with sodium and aluminum from the concentrated extract. Oil shale can be extracted under mild conditions using standard extraction

Figure 6.—Bayer process (Peters and others 1966).
Dawsonite: Its Extraction from Green River Oil Shale

equipment. Little silica will dissolve from the oil shale, eliminating the loss of caustic and alumina to the scale-forming sodium aluminum silicate precipitate which plagues the Bayer process. The moderate temperature and pressure conditions inherent in oil shale processing will minimize water requirements which are large in the Bayer process.

Clarification

Bayer

Separation of the undissolved residue from pressure digestion, called "red mud," is a complex procedure made difficult by the fine-particle product resulting from digestion. Many of the recently published improvements on the Bayer process center on speeding the settling rate of the red mud from the aluminum-bearing solution. Washing the red mud, now accomplished with large series multistage countercurrent mud washers (Reese 1955), is also a difficult procedure.

Oil Shale

The soluble alumina can be extracted efficiently from much larger spent shale particles. Particle size control to retorting and extraction can optimize both the extraction and the separation rate. Particles as small as those generated in the Bayer process [<1µ for some ores (Reese 1955)] need never appear in the spent shale.

Comparison

The spent shale settling equipment will have to handle many times the solids volume that the red mud from the Bayer process represents. However, the spent oil shale is easy to extract to wash and to filter and the possibility of using and maintaining larger particles, and the lower density of the liquor carrying the particles being separated all tend to make spent shale separation much easier than red mud separation.

Precipitation

Bayer

Aluminum trihydroxide is precipitated from the supersaturated "green liquor" by cooling, then seeding the liquor with as much additional aluminum trihydrate as is in the "green liquor." The precipitation is rapid at first, then slows. Total precipitation time is 65 hours, and only 50 percent of the alumina in the liquor is recovered (Peters and others 1966). After the Al(OH)₃ precipitate is removed, the spent liquor is reconditioned and recycled.
Oil Shale

Extracting alumina from spent shale requires only enough excess base to keep the low concentration of aluminate ion in solution. This limited base will neutralize readily on injecting CO₂, and the solution will shortly begin to precipitate Al(OH)₃. Seeding with about 25 percent of the liquor's Al(OH)₃ (Peters and others 1967) may be useful to provide particle size control. Hall and Haas (1970) found this precipitation both quick and nearly quantitative on a laboratory scale. The resulting sodium bicarbonate solution containing only a limited amount of alumina is reprocessed for soda ash recovery and recycling.

Comparison

Aluminum trihydroxide precipitation in the Bayer process is an art, according to Reese (1955). The required temperature control, the long storage time necessary for precipitation, and the density of the residual solution [making Al(OH)₃ separation difficult] indicate that it is also an expensive art. Chemical precipitation of Al(OH)₃ from the spent shale extract is much more likely to be a science.

Additional factors, which may provide alumina extraction from oil shale some economic advantage, include the availability of process materials from the processed ore. Soda ash will be produced routinely from dawsonite even in the absence of nahcolite. Co-occurring nahcolite can provide soda ash, if necessary. If not, the nahcolite may be mechanically separated for use as an SO₂ absorbent (Weichman 1974). The CO₂ required for the precipitation may be obtained from flue gas (Peters and others 1967) or might be recovered from processing the co-occurring nahcolite. Lime for generating the NaOH required could be obtained by firing some of the washed spent shale discard.

Aluminum Metal Production

Nielsen (1969) suggested producing aluminum metal from the oil shale products, burning the oil on site to generate the D.C. electric power required for electrolyzing the alumina. A test balance on energy available for electrolysis can be made using the specimen section described in figure 5. Aluminum metal production, including the heat-up of the molten salt bath, requires up to 13 kilowatt-hours of direct current energy per pound of aluminum metal produced (Shreve 1956). The 1,000-ton alumina yield indicated for 30,000 tons of dawsonite-bearing oil shale per day will yield 529 tons of aluminum metal. Consequently, production of aluminum metal will require 13.8 x 10⁶ kilowatt-hours of electrical energy daily.

The 23,000 barrels per day of shale oil represents 1.38 x 10¹¹ Btu of heat energy. On the basis that 3,412 Btu equal 1 kilowatt-hour, this repre-
sents 40.4 x 10⁶ kilowatt-hours per day from oil combustion. Energy available from the oil appears adequate. However, thermal efficiency of electricity generation is a limiting factor. A thermal efficiency of 34 percent would be required to produce aluminum metal from all the oil produced. Additional energy would be available from the retort gas.

CONCLUSION

Production of alumina from oil shale bearing dawsonite and nordstrandite with simultaneous production of shale oil and sodium carbonates is technically feasible. Advantages in the extraction properties of spent shale may compensate adequately the disadvantage imposed by extracting large quantities of spent shale. Production techniques should be designed around the character of the oil shale, not applied directly from the Bayer process.

REFERENCES


Haas, F. C., and Atwood, M. T., 1975, Recovery of alumina from dawsonitic oil shales: Colorado School Mines Quart., v. 70, no. 3.


