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Some Potential Oil Shale Co-Products
Piceance Basin, Colorado

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Abstract

Based on reconnaissance-level geochemical data and past research results, several valuable mineral products may potentially be produced along with shale oil from the Green River oil shale deposit. These include Nahcolite (now being produced by solution mining methods), Aluminum, Lithium, Gallium, Cobalt, Manganese, Cement, and perhaps others. Collectively, these products could equal to or possibly double the "Raw Rock Value" of 25 gallon per ton oil shale. These value-adding potential products could result in (1) significantly increasing the economic viability of oil shale, and (2) allowing economic production of oil from lower grade shale, thus increasing the recoverable shale oil resource. Present and projected leasing and reported research work on shale oil production does not include addressing recovery of these mineral products (except perhaps Nahcolite). These materials are potentially a very valuable national resource, and a vigorous R&D program is needed to determine the feasibility of their recovery. Like oil shale, their potential value Basin-wide is many trillions of dollars, both in market value and more importantly, in raw material input to our economy.

Introduction

The purpose of this discussion is to draw attention to several potentially valuable additional mineral resources that occur in the oil shale beds, and to the need for R&D to explore the feasibility of their co-recovery with shale oil. Because the costs of the first steps of the classical "mine-grind-refine" ore recovery process would be covered by shale oil, separation and recovery of these resources could be relatively inexpensive.

At present, both oil shale and most of the materials discussed are "resources" (in place, but not currently economical) as compared to "reserves" (economically producible). Currently, nahcolite (sodium bicarbonate) in oil shale is being produced by solution mining methods.

Most of the analyses used herein were done during the 1970s-80s, when demand, use and prices for the resources discussed were much lower than today. The potential "rock value" of these additional in-place mineral products could equal or exceed that of the shale oil from the same "ore."

Assuming that both shale oil and these materials can economically be co-produced, then (1) an overall "oil shale" operation should be significantly more profitable, and (2) oil shale of lower grades could be produced, thus adding perhaps a 100-billion bbl to our total shale "reserves."

The most important "value" of these materials is as domestic input to our economy. The use of aluminum, lithium, and gallium could be much more important in the future.

For a general overview of the geology and other mineral resources in Piceance Basin, see reports by Donnell (1987), Dyni (l987) and Beard et al (1974). Most of the oil shale resource in Piceance Basin is federally owned. It underlies more than 1000 square miles, ranges in thickness from less than 100 feet to more than 2000 feet, and probably averages 20-30 gallons per ton. Most of the resource is a kerogen-bearing marlstone, deposited in a large interior lake system (Eocene) some 50 million years ago. Only oil shale and Nahcolite are recognized under the recent Federal R&D

oil shale leasing program. Recovery of the additional resources discussed herein could only be done by mining oil shale and using surface retorting methods.

Resources

The resources noted below include aluminum, cobalt, gallium, lithium, manganese, molybdenum, and cement. There could well be others, because of recent market prices and because many "black shale" formations world-wide contain unusual concentrations of metallic elements. Reportedly, a few past studies have addressed recovery of magnesium, sulfur, cement, and other products.

Most of the basic data for the numbers used herein are from a compilation by Dean (1976), which contains analytical data from more that 600 samples (from outcrops, cores, mines). These reconnaissance level data were compiled to provide some insight into environmentally important materials that could be present in retorted shale. Desborough and others (1976) compiled trace element data from the Mahogany and R-4 zones in four test holes across the basin. The average values for these four test holes are approximately equal to the average from the several hundred samples reported by Dean (1976). Presumably, co-recovery of several of these materials could lessen unwanted post-recovery environmental effects. Elemental analyses from a Department of Energy study (1981) suggest that elements in area stream sediments are present in similar but somewhat lower concentrations than those in shale noted by Dean. The report includes analyses of several additional elements at concentrations of interest.

Materials

In the following discussion, the "base" raw rock value of 25 gallons per ton shale is about $48/ton (2009 oil price range). Many of the prices noted herein have varied widely during recent years. The values noted for some are crude estimates. Most numbers are rounded, resulting in minor inconsistencies in this text. The "rock values" noted herein are values for in-place "ore."

Aluminum: Light Metals, Alloys – Dawsonite ($NaAlHCO_3$) is about 14% aluminum. Beard, Tait, and Smith (1974) estimated a resource of 19 billion tons of Dawsonite. This resource is mostly in the lower one-half of the oil shale deposit. The dawsonitic shale contains about 6.5 billion tons of alumina (Al_2O_3), and about 2.7 billion tons of aluminum metal. Grade is in the range of about 1-10% Dawsonite, and probably averages 5% or more, or about 14 lbs Al/ton. At $1.50/lb, this could add about $21/ton to the "rock" value of oil shale. The total in-basin resource value may be in the range of 8-10 trillion dollars. Past R&D (Haas & Atwood, 1975) suggests that alumina is readily extractable from some types of retorted shale.

Lithium: Batteries, pharmaceuticals, lubricants - Probably occurs as a carbonate. (Dean 1976). Concentrations are in the range of 5-700 ppm, and average about 70 ppm (0.14 lbs/ton). Recent lithium prices are in the $20 to $40/lb. range and higher, or about $5/ton of "average" shale. There may be about 200 million tons of lithium metal resource in the basin, with a total gross value in the range of 10-15 trillion dollars.

Gallium: Electronics, LED Materials – Mode of occurrence uncertain. Grade ranges from about 2-40 ppm, and averages about 10 ppm, or 0.02 lbs/ton. At a price of $225/lb., this has a range in added average "rock" value of about $5 per ton of ore. There may be about 30 million tons in the basin-wide resource, with a gross raw rock value in the range of 10-15 trillion dollars.

Cobalt: Metal Alloys: Probably occurs with sulfide minerals. Grade ranges from about 5 ppm to about 400 ppm, and averages about 10 ppm, or about 0.02 lbs/ton of shale. Recent cobalt prices are in the $100/lb range, adding from about $1 to $80 per ton of shale. There may be about 30 million tons in the basin-wide resource, with a gross value of about 5 trillion dollars.

Molybdenum: Metal Alloys – Probably occurs with sulfide minerals. Grade ranges from 5-40 ppm, and averages 10 ppm, or about 0.02 lb/ton. At $20/lb, this adds from about a $.20 to $6 per ton of shale. Total resource may be in the range of 30 million tons in basin, with a gross value in the range of a trillion dollars.

Manganese: Metal Alloys – May occur in Dolomite, at concentrations from about 30-2,000 ppm, with an average of about 300 ppm (0.6 lb/ton). At $2/lb, this could add about $1/ton to the value of oil shale. Total resource in the basin is in the range of 800 million tons with a potential value of more than 1 trillion dollars.

Cement: Construction Material – Cement is a potential product from retorted oil shale (Limestone/Dolomite). Limited R&D (Haas & Atwood (1975)) suggests that usable grade cement is readily obtainable from some types of retorted shale. Assuming that 1/10 of the total shale processed is converted to cement, the resource may be about 300 billion tons. Current bulk cement is priced in the $100 to $150 per ton range, for a potential total value in the range of 30 to 45 trillion dollars.

Discussion

Figure 1 is a summary depiction of concentration ranges from Dean (1976). The data are from more than 600 analyses in Piceance Basin and a few dozen analyses from the Uinta and Green River Basins. These latter values do not appear to be such to significantly change the general concentration pattern. Presumably, most of the samples were of *rich* shale (from mines and cores). For purposes of this discussion, the assumption is that rich and lean shale have similar concentrations.

Figure 2 depicts gross *rock values*, assuming a 100,000 BPD shale oil operation using 25 GPT ore (about 170,000 TPD of ore would be mined and processed). Note that the theoretical value of co-products, at "average" rock value, is about equal to that of shale oil. Maximum values could be more than twice that of shale oil.

The concentration range numbers are from Dean (1976) and Beard et al, 1974), the prices are presumed to be within a reasonable 2007-2009 range and the gross rock values are thereby derived. A 100% recovery for all products is presumed, although 50-80% may be more realistic.

The potentially large amounts and values of the "resources" of both oil shale and the above materials clearly justify serious R&D efforts aimed at achieving economic recovery. The potential cash flow from shale oil and co-produced materials could be very large. For example, a 10% royalty stream from a 100000 BPD oil shale plant could be about one million dollars per day.

Future shale oil production rates are not known, but could be in the range of several hundred thousand BPD. The high stakes are obvious, both in royalties and *especially* in raw material input to the Nation's economy.

Some of the above estimated "resources" appear to be a significant percentage of U.S., or even world "reserves" and may be of geo-political significance.

Some R&D Needs

A basic need is to better define the geologic, stratigraphic, and mineralogical occurrence of these resources. Some degree of stratigraphic control of concentration is likely, which could facilitate economic recovery. R&D is needed on recovery methods with a variety of shale oil recovery methods. Consideration should be given to recovery from both pre-and post-retorted shale, and to pre-concentrating an ore stream of perhaps several materials prior to individual resource separation. Some of the elements noted will tend to remain in the "spent" shale, some may in the shale oil, and some in the "off gas" or "exhaust" stream. In addition, an overall R&D effort is needed to lessen the "retorting" energy required for both shale oil and the above-noted resources.

Summary

Because of the enormous size of the resource, and thus the long-term importance to the Nation, research must be aimed at obtaining a high percentage of recovery. The planning must not be unreasonably biased toward short-term considerations that would result in either future loss of resources, or to post- recovery conditions that hinder future recovery of near-total resources.

Selected References

Beard, T. N., Tait, D.B., and Smith, J.W., 1974, Nahcolite and dawsonite resources in the Green River Formation, Piceance Creek Basin, Colorado; in Guidebook to the energy resources of the Piceance Creek Basin, Colorado; Edited by D. Keith Murray, Rocky Mountain Assn. of Petroleum Geologists, pp 101-110.

Dean, W. E., 1976, Geochemistry of Green River Oil Shale: in U.S. Geological Survey Open File Report 76-729, pp 48-56.

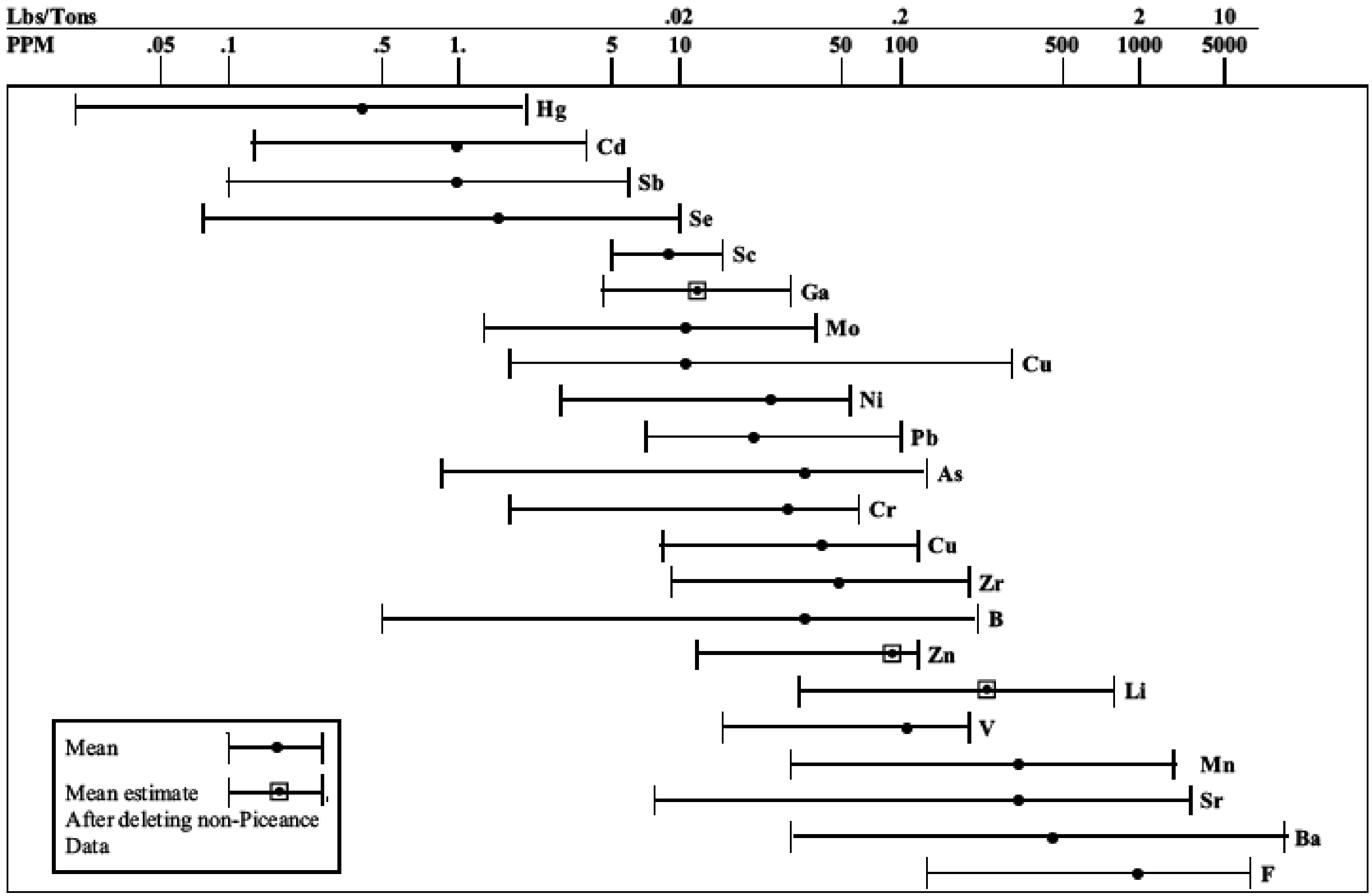
Desborough, G. A., Pittman, J. K., and Huffman, C., Jr.,1976. Concentration and mineralogical residence of elements in rich oil shales of the Green River Formation, Piceance Creek Basin, Colorado, and the Uinta, Utah – A preliminary report; Chemical Geology, Vol. 17.

Donnell, J. R., 1987, Storehouse of energy minerals in the Piceance Basin; U.S. Geological Survey professional paper 1310, pp 21-28.

Dyni, J. R., 1987, The origin of oil shale and associated minerals: in U.S. Geological Survey Professional Paper 1310, pp 13-20.

Haas, F.C., and Atwood, M.R., 1975, Recovering of alumina from dawsonitic oil shale, Colorado School of Mines quarterly, Vol. 70, No. 3.

U.S. Dept. of Energy, 1981, Uranium hydrogeochemical and stream sediment reconnaissance of the Grand Junction NTMS quadrangle, Colorado/Utah.



Modified after
Dean, 1976

Figure 1 **MINOR ELEMENTS IN OIL SHALE PICEANCE BASIN, COLORADO**

Figure 2

OIL SHALE, PICEANCE BASIN POTENTIAL CO-PRODUCTS

100,000 BPD, 25 GPT
170,000 TPD Mined

	Concentration ppm or %			Lbs/Ton			Price	Gross Rock Value, $/T			Potential Gross Revenue Millions Dollars per day		
RESOURCE	Low	Avg	High	Low	Avg	High		Low	Avg	High	Low	Avg	High
DAWSONITE (AL) %	**1**	**5**	**10**	**3**	**14**	**28**	**$1.25/lb**	**3.75**	**18**	**35**	**0.62**	**3**	**5.8**
LITHIUM PPM	**4**	**75**	**800**	**.008**	**.15**	**1.6**	**$30/lb**	**0.24**	**4.5**	**48**	**0**	**0.75**	**3**
GALLIUM PPM	**2**	**10**	**40**	**.004**	**.02**	**0.1**	**$225/lb**	**0.9**	**4.5**	**18**	**0.15**	**0.75**	**3**
SUBTOTAL								**4.9**	**27**	**101**	**0.77**	**4.5**	**12**
CEMENT	**10,000 TPD**						**$120/ton**	**120**			**1.2**		
NAHCOHLITE	**10,000 TPD**						**$120/ton**	**120**			**1.2**		
SHALE OIL	**25 Gallons per Ton**						**$80/bbl**	**48**			**8**		
Total Oil and Co-Products, $ Millions /Day											**11**	**15**	**22**

NOTE: Cr, Co, Cu, Mg, Mn, Mo, Ni and V occur as generally lower values.
Their combined recovery could add from about $100,000 to $5,000,000/day.