①
50181
①
49 DTLS
I-104
UCID-19208

MASTER

AN APPROACH TO RECOVER
STRATEGIC METALS FROM BRINES

Ellen Raber
Jack Harrar
David Gregg

September 16, 1981

Lawrence
Livermore
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

AN APPROACH TO RECOVER STRATEGIC METALS FROM BRINES

ABSTRACT

The objective of the proposed research is to evaluate hypersaline brines from geothermal sources and salt domes as possible sources for some "strategic" metals. This research is suggested because several previous analyses of brine from geothermal wells in the Imperial Valley, California, and from Gulf Coast salt domes, indicate near commercial values for platinum as well as other metals (i.e. gold, silver). Extraction of the platinum should be technically feasible. A research program should include more complete systematic sampling and analysis for resource delineation, followed by bench-scale investigation of several potential extraction processes. This could be followed by engineering feasibility and design studies, for extraction of the metals either as a by-product of other operations or in a stand-alone process.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

"Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48."

Peay

INTRODUCTION

Recently there has been considerable interest in insuring reliable sources for what are considered to be strategic metals. The identification of the most critical metals is not as simple as might be first perceived. It depends greatly on the particular situation, especially whether we are at war or not. In peacetime, the most critical metals are chromium, cobalt and nickel. However, in wartime, this list is extended to include platinum, niobium, (columbium), tantalum, beryllium, germanium, manganese, titanium, and possibly others.

The strategy for securing a reliable source of a valuable metal might be quite different in peacetime vs. wartime. In peacetime, the mere threat of a permanent substitution if a particular metal source is interrupted could be sufficient to discourage too much manipulation if the producers also want a reliable market for their product. Thus, a perceived substitution capability could suffice as a counter threat. However, the situation could be quite different in wartime. One would then want to have a reliable domestic source, even if the product cost was higher than the prevailing world market (or what used to be the prevailing world market). Of these metals which are commonly listed as "strategic", cobalt and the platinum group metals are particularly vital because of their important uses and the U.S. dependence on supplies from unstable sources (i.e., Southern Africa, Soviet Union).

OBJECTIVE AND BACKGROUND

The proposed research is directed towards evaluating the feasibility of domestically producing at least one of these strategic metals, platinum, along with gold and silver from brines. Platinum is an important catalyst in petrochemical processes and in automobile pollution-control devices. It is

possible that other metals could also be recovered, but further analysis is required to determine this. In particular, we are considering recovery of metals from both hydrothermal geothermal brines and from brines created by leaching salt domes. In both these cases the metal recovery would be a by-product. The primary uses (the production of electric power, or the creation of large, underground storage caverns) should pay for the primary cost of the overall operation. However, the potential does exist for economic conditions occurring in which metals recovery from these sources may be the primary operation.

The geothermal brines of primary interest are those in the Salton Sea Geothermal Field, Imperial Valley, Southern California. An experimental pilot plant has been operated in this area to evaluate the feasibility of producing power from these brines. A small commercial power plant is also operating with brine from a similar, nearby resource, and others are in the planning stages. However, it appears that there are still sufficient problems, primarily related to the reinjection of the cold spent brine and scaling, to retard large-scale commercialization. These problems are still being worked on, and when they are satisfactorily resolved, the resulting commercial power use of these brines will also provide a very large supply for metal extraction.

Salt dome leaching is presently being employed to create large underground caverns for a variety of storage applications. The use of greatest recent interest is to provide storage for the Strategic Petroleum Reserve. However, other applications have been investigated such as caverns for gas storage, and for storing hazardous wastes. Almost anything that requires large volume storage might employ such leached salt caverns. Therefore, there is good reason to believe that there will be an expanding activity in this area in the future. This in turn will provide corresponding expanded opportunities for potential metals recovery.

At Lawrence Livermore National Laboratory we have been working with brines for several years in our Geothermal and Strategic Petroleum Reserve Programs. Specifically, the work has been primarily directed towards the chemical conditioning and filtering of the brines to prepare them for subsurface reinjection as a means of disposal. As a necessary part of this program, we conducted an extensive study of the chemical properties of the brines. The primary emphasis was to determine the major chemical constituents in order to establish processing requirements necessary to prepare them for reinjection. Some trace constituents were also identified at this time. The resulting chemical analyses showed that the brines contained significant (trace) concentrations of platinum, gold, silver and possibly other valuable metals. These analyses indicate to us a possible, partial solution to the strategic metals problem.

CHEMICAL ANALYSES OF THE BRINES

The general analyses of these brines is presented in Table 1. These analyses were made on filtered samples (0.4 μ m filter) by a combination of three different techniques: ICP (inductively coupled plasma emission spectroscopy), atomic adsorption spectrophotometry, and ion selective electrodes. The results of these analyses, as extensive as they are, are still not complete. However, they do show that the brines contain a wide variety of interesting materials in concentrations that are far greater than exist in sea water.

At the time that the analyses in Table 1 were made, we had no particular interest in Pt, Au and Ag, and the analytical techniques employed were not sufficiently sensitive for these metals. However, we later suspected that such heavy metals might be concentrated in a number of evaporative deposits, such as salt dome-type deposits, and had the brines analyzed specifically for

Table 1

Analyses of Various Brines (ppm)

Element	Geothermal		Strategic Petroleum Reserve	
	Magmamax 1	Woolsey	Bryan Mound	West Hackberry ^a
Li	127	138	0.7	-
Na	41,000	42,400	123,648	121,762
K	5,500	6,900	298	15
Mg	88	81	14	8
Ca	17,900	21,700	921	319
Sr	303	299	2.4	2.
Ba	150(est)	150	-	-
Fe	97	215	0.45	1.0
Cu	1.24	2.0	1.	0.03
Mr	417	607	0.2	.004
Pb	33	43	2.	.1
Zn	168	226	1.4	0.133
Si as SiO ₂	456	510	2.	-
Al	2.3	3.4	1.	-
As	11.7	13.5	5.	-
B	373	409	2.	-
Cd	1.3	1.5	2.	.002
Co	0.3	0.3	0.2	-
Mo	8.0	8.6	0.7	-
Ni	0.4	0.4	0.5	.004

Table 1 - (Continued)

Element	Geothermal		Strategic Petroleum Reserve	
	Magmax 1	Woolsey	Bryan Mound	West Hackberry ^a
P	15	15	10.	-
Ti	1.4	1.4	0.1	-
V	0.45	0.64	0.2	-
Zr	0.31	0.39	0.5	-
SO ₂ -	41	89	3000	1,900

^a Analyses by EPA

these three metals.

Two samples of brine, one from the Magmamax No. 1 well (Salton Sea Geothermal Field) CA., and one from Cavern 2 at Bryan Mound, LA (Strategic Petroleum Reserve), were evaporated to dryness, and the solids analyzed for silver, gold and platinum. Brine obtained from Bryan Mound was ultrafiltered to $0.01\ \mu\text{m}$ prior to evaporation and analysis.

The analyses (Table 2) were carried out by Ledoux Laboratories of Teaneck, NJ, which specializes in precious metal fire assays. Reported sea water analyses are also presented for comparison purposes. According to this laboratory, the quantities of the metals determined were near the detection limits for the procedures used. Ledoux states that their results for Pt are correct to within five percent. The Au and Ag values are good to within about ten percent. The Ag value reported for Magmamax No. 1 brine is in excellent agreement with our own previous (ICP) analyses. This suggests that the Ag values reported for Bryan Mound are probably also reasonable.

We do not know the origin of the heavy metals. The metals might be indigenous to the salt (i.e. blue halite) or phases contained within or associated with the salt. Their source possibly could be from rising sea-bed volcanics in areas of sea-floor spreading. The Salton Sea is astride the landward extension of the East Pacific Rise, and spreading is likely in parts of the Gulf of Mexico Basin.

Table 2

Results of Analyses of Brine Solids for Precious Metals

	<u>Measured Concentrations in Solids, ppm^a</u>		
	<u>Ag</u>	<u>Au</u>	<u>Pt</u>
* Magmax No. 1	2-3	0.4-0.5	0.2-0.3
* Bryan Mound	2-8	0.5-0.7	0.2
	<u>Calculated Concentration in Brine, ppm</u>		
	<u>Ag</u>	<u>Au</u>	<u>Pt</u>
* Magmax No. 1	0.5-0.7	0.1	0.06
* Bryan Mound	0.6-2.7	0.2	0.07
(Seawater Analyses)	3x10 ⁻⁴	4x10 ⁻⁶	(present in Marine organisms)

^a34 ppm = 1 oz/ton

*Fire assays

ESTIMATED RESOURCE SIZE AND VALUE

I. Strategic Petroleum Reserve (SPR)

DOE's Strategic Petroleum Reserve Program, enacted April 18, 1977, provides for the storage of as much as one billion barrels of crude oil to offset the immediate effects of a severe disruption in the normal supply of imported oil.(1-2) Five underground storage sites in Texas and Louisiana were initially selected for oil storage because of their availability and their proximity to interstate oil pipelines and tanker ports. One of these SPR sites consists of mined near-surface dry chambers; the others are deep water-leached caverns in subsurface salt domes.

In order to store one billion barrels of crude oil in such salt domes, an equivalent volume of salt must be removed. This would correspond to a removal of 3.44×10^{11} Kg of salt. Assuming average values of concentration for Au, Ag and Pt and assumed nominal values, the following table can be generated.

Table 3
Projected Mineral Values from SPR Brines

<u>Metal</u>	<u>Concentration</u>	<u>Total Quantity</u>		<u>\$/Troy Oz.</u>	<u>Total Value</u>
	(ppm)	(Kg)	(Troy Oz.)		(\$)
Ag	5	2×10^6	6×10^7	12	0.7×10^9
Au	0.6	2×10^5	7×10^6	500	3×10^9
Pt	0.2	7×10^4	2×10^6	500	1×10^9
					Total 5×10^9

Compare this projected value to the total value of the oil stored. If one assumes that the oil is purchased at \$30/bbl, then the total oil cost is $\$30 \times 10^9$. Thus, the potential metals recovery value is approximately 17% of the value of the stored oil. This is certainly a very significant fraction of the oil cost and justifies further investigation.

II. Salton Sea Geothermal Brines

It has been estimated that the geothermal energy resources of the Salton Sea Field are capable of producing 500-3,600 MW for 20 years.⁽³⁾ It is also estimated that a fluid flow of 10^5 pounds of brine/hr is required to produce one MW of electricity. This corresponds to a potential brine production from

8.8 to 63×10^{12} pounds over the life of the field. Assuming average values of concentration for Au, Ag and Pt, the following table can be generated.

Table 4
Projected Metal Values from Geothermal Brines

<u>Metal</u>	<u>Concentration</u>	<u>Total Quantity Range</u>	<u>\$/Troy Oz</u>	<u>Total Value Range</u>
	(ppm)	(Troy Oz.)		(\$)
Ag	0.6	$8-50 \times 10^7$	12	$1-6 \times 10^9$
Au	0.1	$1-9 \times 10^7$	500	$5-40 \times 10^9$
Pt	0.06	$8-50 \times 10^6$	500	$4-20 \times 10^9$
				Total $1-7 \times 10^{10}$

Compare this number with the total value of the electricity generated. If we assume that the electricity is valued at 5¢/Kwh, then the value of electricity is from $\$4.4-31.5 \times 10^9$. The value of the metals exceeds the value of the electric power; thus recovery of the minerals may help make this geothermal power production in the Salton Sea area economically feasible.

PROPOSED RESEARCH PROGRAM

I. 1st Phase: Chemical Analysis of Representative Samples:

The initial phase of the program would be directed toward confirming and extending the chemical analyses of the brines. This is necessary not only to establish the accuracy of the chemical analyses, but also to obtain a sufficient number of samples to insure a representative view of metal/mineral

concentration changes (if any) as a function of location and time during leaching or extraction. Concisely, this would involve the following four steps:

- 1) Obtain detailed information concerning ongoing operations in leaching cavities for the Strategic Petroleum Reserve as well as potential plans for Salton Sea geothermal production.
- 2) Obtain available geological information about both areas.
- 3) Obtain representative brine samples from several sites and analyze them for metals of interest. Interpret this information in combination with 1 and 2 above.
- 4) Attempt to identify additional resources that might have similar potential.

II. 2nd Phase: Investigation of Several Techniques for Metals Recovery

Due to the extremely low concentrations, some research is necessary to identify the best extraction technique and to quantify how well it will perform. Initially, we will conduct bench-scale studies to quantify and compare the following metals recovery techniques:

- 1.) Evaluate the reducing borane-amine resins AMBORANE 345 and 355 being produced by the Rohm and Haas Company. This material appears to be an unusually attractive potential extraction agent for precious metals, but may require that the water be relatively free of dissolved oxygen. This would make it very useful for geothermal brines although, not as effective for the SPR brines. These resins exhibit a high degree of selectivity for Pt, Au, Ag, certain metal ions, especially precious metals, reducing these ions to the free metal (zero oxidation) state. (4-5)

2.) Evaluate various activated charcoals, which are known to act as reducing agents for gold and silver and have shown good recovery at higher concentrations. Studies in the field of metallurgy have indicated reasonably good adsorption of many metallic compounds on activated carbon. On a pilot plant scale, adsorption and removal for some metals (i.e. chromium, silver) was shown to be greater than 99% in most experiments. (6)

3.) Evaluate electrowinning processes starting with what appears to be an attractive system called an "Eco-Cell" produced by the Belco Pollution Control Corporation. This process has three distinct advantages: (1) the process operates successfully with very dilute solutions, (2) the anodes are in a controlled environment and separated from the cathode compartment by ion exchange membranes eliminating severe corrosion problems, and (3) the process produces metal powder continuously, easily recovered in conventional liquid cyclone equipment. (7)

4.) Evaluate selected ion exchange resins as they are identified.

5.) Evaluate a new process being employed with considerable success by the "Uranium from Sea Water" program at LLNL. This process consists of adding to the water chelating agents which attach to the metal of interest. The complex is then sorbed from solution with activated carbon. Considerably enhanced adsorption coefficients on activated carbon have been achieved for the case of the uranyl ion, and it is possible that similar sorbing agents can be identified.

III. 3rd Phase: Engineering Design

After phases 1 and 2 are well along, engineering feasibility studies should be initiated. Such initial engineering should be started before the completion of phase 2 since the early engineering information can then be fed

back into this preparatory work to help guide it. Finally, we would plan to design and build a pilot plant for extraction of the metals.

REFERENCES:

1. Energy and Technology Review, Lawrence Livermore Laboratory, August, 1979, Pg. 1.
2. R. Davis, "National Strategic Petroleum Reserve," Science, vol. 213, August, 1981.
3. L. Younker and P. Kasameyer, "A Revised Estimate of Recoverable Thermal Energy in the Salton Sea Geothermal Resource Area," Lawrence Livermore Laboratory Rept. No. UCRL-52450, April, 1978.
4. Rohm and Haas Company Report, "Amborane 345 Reductive Resin," DIC-79-2, June 1980.
5. Rohm and Haas Company Report, "Amborane 355 Reductive Resin," DIC-79-3, May 1980.
6. A. Netzer and J.D. Norman, "Removal of Trace Metals from Wastewater by Activated Carbon," Department of Chemical Engineering, McMaster University, Hamilton, Ontario.
7. Belco Pollution Control Corporation Report, "ECO-Cell, for Metals Extraction and Recovery by a Continuous Electrolytic Process," U.S. Patent No. 4,028,199.