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BUREAU OF MINES - - DEPARTMENT OF THE INTERIOR.

BUREAU OF MINES INVESTIGATES GOLD IN OIL SHALES AND ITS POSSIBLE RECOVERY.

By Thomas Varley (Superintendent, Intermountain Station, U.S. Bureau of Mines)

For a year or more, statements have appeared in the technical press, and especially in various trade journals, indicating that valuable metals such as gold, silver, platinum, and other rare metals, have been found and also have been successfully extracted from oil shales. These reports stated that decarbonization and special methods of chlorination treatment, leaching and subsequent precipitation, also cyanidation followed by table concentration of the residues after cyanidation, all indicated that gold and silver and other metals could be, and were, successfully recovered. Such articles have caused much misunderstanding, and as the correctness of some of the statements made in them were questioned by some of the technical journals and by various chemists and metallurgists, an investigation of the subject was begun by the metallurgical division of the Bureau of Mines, in order, if possible, to determine to what extent, if any, metals of value do occur in oil shales, and if so, the feasibility of attempting their recovery by the processes said to have been used for that purpose.

Inasmuch as the Bureau's station at Salt Lake City is investigating the recovery of oil from oil shales, the investigation of the recovery of metals from oil shales was assigned to my direction as superintendent of that station. An agreement had been entered into with the owner of an extensive oil shale deposit in Wyoming whereby I would personally collect the samples of shales for use in the investigation.

Before beginning the work at Salt Lake City, a study was made of the process used by A. M. Beam of Denver, Colorado, for the extraction of metals from oil shales. I then visited the mill of the American Continuous Retort Co., which is situated near the assay office of A.M. Beam. In the crushing department of the plant there was a considerable amount of oil shale, which apparently had been unloaded from a car, ready for treatment. The plant originally had been used by the Chamberlain Ore Concentrating Co., as a sampling mill and concentrator, and the equipment therein consisted of the usual equipment found in such mills. The plant had been further equipped for oil-shale experiments with a three-hearth retort for oil extraction, and another retort constructed especially for decarbonizing the spent shale, a rod mill was used for crushing the spent shale after the oil had been extracted therefrom. The decarbonized shale was, according to Mr. Lewis, president of the American Continuous Retort Co., treated in hot solutions agitated in pachuca tanks which were equipped with amalgamation plates. After a batch of ore had received this treatment for a sufficient length of time, the material was treated by cyanidation and the solutions from the cyanide leaching were passed through zinc boxes where any gold or silver that might have been taken into solution by the cyanide would be precipitated.

The residues after cyanidation were pumped up to another floor and passed over a Wilfley table. This table and the cyanide boxes were the only part of the plant in operation during my visit. I observed on the table a concentrate which I distinctly identified as lead, probably a little iron and zinc, and some black material which was probably pyrite which had been altered during the roasting and decarbonization. There was a very thin gray streak on the table which I could not identify, although it probably might have been either lead sulphate or lead carbonate. The presence of lead and zinc on the table led me to believe that there must have been some of this material remaining in the elevators or pump boxes. This, no doubt, accounted for the presence of the lead and zinc which was supposed to have come from the oil shale, for it is difficult to conceive how such material would be present in crude oil shale.

Mr. Lewis also showed me several pieces of flakey gold which he stated had been picked off the table. Under the microscope this material had the appearance of gold, but it was associated with quartzite. I was handed a small piece of this material, which was picked off the table in my presence. Later this was tested with nitric acid and dissolved; the tests indicated that it was practically all copper. However, it is believed that the piece examined under the microscope contained gold, but I do not know and therefore cannot say it was concentrated from the shale by the Wilfley table.

Procuring of Samples from Green River, Wyoming.

I arrived in Green River, Wyoming, on the morning of May 2, 1922, and Mr. Himes provided every possible convenience to secure the samples of shale. He had two miners and cars ready, also an engineer who had made surveys on his properties. The party then went a short distance northwest of Green River, and we went up on the shale deposits and pried down with bars pieces of shale from several places. These were sacked up under my supervision and expressed to Salt Lake City. I arrived in Salt Lake City, Wednesday, May 3, and the shale arrived late the same afternoon.

Experiments in the Oil-Shale Laboratory, U.S. Bureau of Mines, University of Utah, on the Green River, Wyoming, Shales.

Personally Supervised by Lewis C. Karrick, Assistant Oil-Shale Technologist, U. S. Bureau of Mines.

Upon the receipt of the samples at the Bureau's station at Salt Lake City, they were turned over to Lewis C. Karrick, who conducted the distillation tests. Dr. Frederick Salathe, formerly a chemist with the Standard Oil Co., who had been working on the oil-shale problems connected with the recovery of oil from the shale, and who had been investigating the recovery of metals from the shale in laboratories at Fort Wayne, Indiana, was detailed by Mr. Himes to assist in this investigation, and gave general directions of procedure. The sample was crushed to pass a $\frac{1}{4}$-inch screen. All the material was then thoroughly mixed and the entire batch was quartered down to obtain a 25-pound sample for analysis. This 25-pound sample was distilled in several batches in the Bureau of Mines' assay retorts. The rate of distillation was such that the oil was reduced in all cases in about two-hour distillation periods. The spent shale was retained for further experiments. The oils were tested and gave the following results:

Yield	25 gallons per ton
Specific Gravity	.910
Melting Point	31.2° C
Unsaturation	49.2
Amount of Distillate from Crude	33.2%
Index Value for the Oil	16.4
Index Value for the shale	4.07

The index value of an oil is a quantity calculated from the analytical data of the oil, and is the product of the percentage of distillate to 275°C obtained from the crude oil, and the saturation of this distillate to 275°C.

Amount topped.	Distillate to 275° C.	Per cent Distillate to 275 C.	Per cent Unsaturation	Per cent Saturation
50 cc	16.6 cc	33.2	49.2	50.8

Index of oil = 33.2 x 50.8 = 16.4

The index value of the Shale is the product of the oil yield in gallons per ton of shale and the index value of the crude oil.

16.4 x 25 = index value of shale.

After the shales had been retorted, Dr. Salathe, who had been present during the retorting process, gave instructions as to the procedure to be followed in the treatment of the residues. This is clearly shown in the accompanying diagram or flowsheet of the entire experiments.

The spent shale was pulverized so that all would pass a 40-mesh screen. The pulverized material was then decarbonized under the direction of Dr. Salathe, by the Bureau's analyst and assayer. This was done by heating in a large gas-fired muffle in the fire-assay laboratory. Particular attention was given to see that the temperature within the furnace did not exceed 600° C. at any time during the carbonization. In order to insure this temperature not being exceeded, pyrometers measuring the temperatures were used continuously during the decarbonization treatment. After the entire batch was decarbonized, the material was divided into three parts; part one consisting of 2500 grams was turned over to one of the Bureau's ore-dressing engineers for concentration tests which are given elsewhere in this report. Part two was also turned over to the same engineer for cyanidation tests, and another equal part was retained for the chlorination test.

Chlorination Test.

The portion set aside for this experiment was treated under the direction of Dr. Salathe, in a small rotary retort in the oil-shale laboratory. This was especially desirable equipment for the reason that proper heating and agitation could be procured, allowing the chlorine gas to react on the material properly. The retort was maintained at a temperature of approximately 300° C. throughout the chlorination treatment. In each test about one hour was required to complete the absorption of the chlorine gas by the shale. The chlorine was drawn from a cylinder and then passed through a sulphuric acid solution and led into the retort through a special gas-tight fitting. The gas was liberated at the back end of the shale container, and any excess chlorine and also any voluble gases or vapors liberated escaped from the retort through the delivery tube which led into a gas-washing bottle containing pure water.

Four 1-pound samples were treated identically, and were ultimately bulked together into one composite sample. The delivery tube from the retort, as well as the connections to the wash bottle, were all cleaned with a dilute hydrochloride acid solution. The washings were added to the composite shale sample and enough water added to procure an even mixture. This mixture was agitated for an hour on the rolls and was then filtered through a suction filter.

During the filtering about 12 washes were given the residue, the last few washes being with hot water. The filter cake was then broken up in fresh water slightly acidulated, and after thorough mixing was refiltered and washed. The filtrate was evaporated down to about 500 c.c., enough acid added to give a faint acid reaction and C. P. zinc was added (gold free). The residual zinc was filtered off, washed with dilute hydrochloric acid several times, the residue melted with test lead, then scorified until zinc free, and finally cupelled in the usual way.

In order to obtain a check on the work and to get comparative values on other shales, a sample of spent shale from Soldiers Summit, Utah, was treated in a similar manner to the Wyoming shale by parallel tests, each shale receiving identical treatment.

Recovering by Chlorination.

	Wyoming Shale	Utah Shale
Sample Taken Pounds	4.0	0.88
Sample Taken Assay Tons	61.8	13.7
Gold Content, oz. Gold per ton decarb. shale	0.03	0.02
Gold Content of sample Milligrams	1.85	0.27
Gold Recovered by chlorination Milligrams	0.06	0.02
Per cent of total gold Recovered	3.2	7.4

Discussions of Results.

On calculating the amount of gold actually recovered as a result of the chlorination and leaching tests, it indicates that only 3.2 per cent of the total gold in the crude shale was recovered by this method. It would, therefore, seem that such a treatment would not be profitable as a method of recovering the gold, even though commercial quantities actually existed in the shale.

Methods of Assaying Oil Shales for Gold and Silver.

This phase of the investigation was placed under the immediate direction of Charles G. Maier, consulting chemist for the Bureau, and a member of the technical staff of the metallurgical research department of the University of Utah. It is usually claimed by those who report gold in oil shale and its residues after distillation, that the gold is not determinable by a conventional fire assay, but that special treatment is necessary to recover the gold either for assay or practically. In discussing this matter with Dr. Salathe, it seemed that his idea was that the gold might exist as a colloidal suspension in the oil of the shale, and the presence of sulphur and organic sulphur compounds might enable the gold to distil off during heating and thus cause low assay values to be obtained.

Since it was desirable, in order to calculate the recovery of gold by any extraction method, to know the actual total gold content of the original material, experiments were carried out to show whether the usual fire assay method actually did give low results and to indicate where, in the processes carried out (as above described by Mr. Karrick) it would be possible to lose gold. The tests were performed as follows:

1. Fire assays by the usual methods of raw, spent, and decarbonized* Wyoming shale samples, and spent and decarbonized Utah shale. No raw Utah shale sample was available.

2. A special assay, by a method described below which eliminated possibility of volatilizing gold, on the raw Wyoming shale.

3. The determination of the gold recovered in the chloridizing leach liquors, as above described, obtained by Mr. Karrick.

Methods for 1:

Four samples of $\frac{1}{4}$-assay ton each were fused with the regular flux used for oxidized ores, the four buttons from each sample combined, scorified, and cupelled in the usual manner.

Methods for 2:

The organic matter in a raw shale sample was completely destroyed by chromic acid, all gases given off by the oxidation being washed to prevent loss. No external heat was used. The procedure was as follows: One assay ton of raw shale was placed in a liter flask provided with a separatory funnel inlet, and an outlet tube passing a catch bottle and a wash bottle. The flask contained 25 c.c., of water at the start. 100 c.c., of concentrated sulphuric acid was added through the funnel (the apparatus being kept closed during the run), then 100 c.c., of saturated chromic acid solution were added in small portions, as limited by the course of the reaction in the flask. After the action had for the most part ceased, 25 c.c., more of chromic acid were added, and the whole allowed to digest over night. In the morning, the contents, now completely deprived of organic matter, were diluted with water, and the colorless residue filtered out for assay. The filtrate was treated with excess ferrous sulphate to precipitate any dissolved gold, refiltered, and the ignited papers added to the previous residue. 29.2 grams of raw ore gave a residue of 16.0 grams. The residue was washed free of chromium by repulping with dilute hydrochloric acid, and finally dilute sulphuric acid.

Method for 3:

The leach liquor from chlorination was treated with gold-free zinc dust, the residual zinc filtered off, washed with dilute hydrochloric acid several times, and the residue melted with test lead and scorified until zinc free, then cupelled in the usual way.

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* See Mr. Karrick's statement for method of decarbonization.

The results obtained in these tests are shown in tabular form below:

Gold Content. Oz. per ton.

	Wyoming Shale		Utah Shale	
	As Determined	Calculated to raw shale 30% shrinkage	As Determined	Calc. to raw shale, 30% shrinkage
Raw shale:				
Straight assay......	0.03	0.2		
Special assay......	0.02	0.2		
Spent Shale.............	0.04	0.028	0.01	0.007
Decarbonized Shale......	0.03	0.021	0.03	0.014
	Average	0.022		

Discussion of Results:

In view of those results it is concluded:

A. That the samples tested contain minute amounts of gold, to the extent of possibly 40 or 50 cents per ton of original shale, but the amount found is not of commercial value.

B. That no special precautions are necessary in assaying shale for gold, and that any direct assay by a reliable method will give the true gold content of the original material.

C. That there is no loss by volatilization in these samples either during the distillation of the oil or during further heating and decarbonization, which is greater in amount than the limiting accuracy of a gold assay at its best.

D. That the chlorination treatment of decarbonized shale was totally unsatisfactory as to recovering what little gold is present.

E. That the original shales tested do not show sufficient gold to make it worth while to attempt to recover it.

Table Concentration Tests on Decarbonized Oil Shales from Green River, Wyoming, and Soldiers Summit, Utah

(By James T. Norton.)

Wyoming Shale - Table Test.

Twenty-five hundred (2500) grams of decarbonized oil-shale from Green River, Wyoming, were concentrated on a small laboratory size Wilfley table. The 1st, 2nd and 3rd cuts or concentrates from the first tabling were recleaned by retabling. The products from the second tabling were dried, weighed and assayed. The result of the test is as follows:

	Wt. in Gm.	Assay, oz. per ton Au.	Per cent Recovery Au.
Heads	2500.0	0.03	100.0
1st Cut Conct.	35.7	0.46	21.6
2nd Cut Conct.	49.2	0.10	6.6
3rd Cut Conct.	166.5	0.035	7.8
2nd cleaner tailing	600.0		
1st rougher tailing	1595.0		
	2446.2		

As the heads on this material are very low in gold content, the tailing products were not assayed. The recovery is very good, considering the material treated.

Utah Shale - Table Test.

Twenty-five hundred (2500) grams of decarbonized oil-shale from Soldier's Summit, Utah, were concentrated on a small laboratory size Wilfley table. The 1st, 2nd and 3rd cut or concentrates from the first tabling were recleaned by retabling twice. The products from the third tabling were dried, weighed and assayed, the products from the 1st and 2nd cuts being combined for assay. The results of the test is as follows:

	Wt. in Gm.	Assay, oz per ton Au.	Per cent Recovery Au.
Heads	2500.0	0.02	100.0
1st cut	6.5)	53.7 - 0.05	5.4
2nd cut	47.2)		
3rd cut	91.0	0.01	1.8
2nd and 3rd cleaner tailing	855.0		
1st rougher tailing	1505.0		
	2504.7		

The tailing products from the test were not assayed as it is obvious that they would be very low in gold, even though a very small amount of the gold was recovered in the concentrate..

Cyanide Tests on Decarbonized Oil Shales

Wyoming Shale - Cyanide Test.

Five hundred (500) grams of decarbonized oil shale ground to minus 40 mesh were agitated on the rolls with 1500 c.c. of a ¼ per cent sodium cyanide solution for 114 hours.

Titrating the solution before and after using indicated that very little of the cyanide had been consumed. The pulp was filtered and washed three times, and the filter cake dried. An assay was not made on the tailing product, as it is obvious from the head assay made on the material being cyanided, that it contained very little gold.

Utah Shale - Cyanide Test.

Three hundred (300) grams of decarbonized oil shale ground to -40 mesh were agitated on the rolls with 900 c.c. of ¼ per cent sodium cyanide solution for 114 hours.

Titrating the solution before and after using indicated that very little of the cyanide had been consumed.

The pulp was filtered, washed three times, and the filter cake dried and weighed. However, assays were not made on the tailing product, as head assays made after the cyanide test had been started, on a sample of the material being cyanided, indicated that it contained very little gold, hence it was unnecessary to determine whether the cyanide had extracted the gold.

Conclusions:

As a result of concentration and cyanidation tests, it is obvious from the head assays made from the samples of decarbonized shales, that under no conditions could the recovery of gold be made commercially feasible, due to the small amount of gold contained in the oil shales. The Green River, Wyoming, decarbonized oil shale assayed, .03 ounce of gold per ton, or 60¢ per ton. Calculated back to the crude shale, which has a shrinkage of approximately 33.3% during retorting, the actual crude value of the shale would be only slightly more than 40¢ in gold. The Soldier Summit, Utah, decarbonized shale assayed .02 ounce gold per ton, or 40¢ per ton. This converted back into the crude shale would be slightly less than 30¢ in gold value per ton.

Microscopic Examination of Oil Shale from Green River, Wyoming, from the Property of J. E. Himes.

(By R. E. Head, Microscopist, U. S. Bureau of Mines.)

The samples examined were taken at random from material used in making the tests previously described, and are sufficiently representative of the entire lot tested to convey an accurate idea of the occurrence and distribution of the sulphide constituents of the shale. The samples were polished and examined by the usual methods applied to microscopic examination of ores.

Polished sections of oil shale, when examined under the microscope, show few of the characteristics observed in thin sections, but the presence of metallic substances is more readily detected due to the reflection of light from their polished surfaces. At a magnification of 106 diameters the existence of pyrite in the Green River shale may be conclusively determined. The mineral occurs in minute particles and grains, and appears to be quite uniformly distributed throughout the samples examined. The pyrite grains are distributed in such a manner that the stratified character of the shale is clearly apparent, and examination of thin sections of shales has shown that tge pyrite is associated with the silica and calcareous components of the shale which form alternate layers with the kerogen and thus give the banded appearance characteristic of the shale family. At the magnification given, numerous particles of pyrite can be detected but they are of so extremely small that they resemble minute glints of reflected light. These small particles appears to be more uniformly distributed than the larger grains described, and when examined at a magnification of 700 diameters, numbers of them are visible in practically every siliceous area in all of the specimens studied. The approximate average size of these small particles is placed at 0.01mm, but it is obvious that particles both larger and smaller than this dimension occur in this group.

No gold was seen in the material examined, which is not surprising when one considers the relatively small content found in the Green River shale. The form in which gold exists in the shale is an open question, and it is probable that the time spent in determining this point would scarcely be warranted, since the amount involved is too small to represent a commercially recoverable product. It is possible that the gold occurs in the "flour form" as very finely divided particles similar to that found in some placer deposits. On the other hand, the presence of pyrite suggests the possibility that it may be of the gold-bearing variety. Either or both of these theories appear logical, and since it has been shown that gold occurs in oil shale, although in a very small amount, it appears possible that exploitation of the shale deposits may result in the discovery of areas of which the gold has been sufficiently concentrated by Nature to be of commercial importance.

General Conclusions.

I. If gold actually exists in oil shales, it can be determined accurately by the ordinary accepted fire-assay method.

2. The Bureau's investigations have proved that by cyanidation and chlorination treatment, only a small percentage of the total gold shown by fire-assay methods on the crude shale is actually recovered by these methods. In other words, the total amount, even though small, shown by such methods, is materially less than indicated by ordinary fire methods, and it is evident that even though the shales did contain gold in commercial quantities, cyanidation treatment and chlorination treatment would not recover sufficient to make the proposition commercially feasible.

3. If there is a possibility of the organic matter in the raw shale interfering with the fire assay of gold and other precious metals, this can be overcome and all dangers of loss avoided by removing the organic matter with chromic acid.

4. The sample of shale from Green River, Wyoming, assayed 3.58% iron. Photomicrographs showed clearly that pyrite is disseminated throughout the shale. This may be more or less responsible for the small amount of gold found in the shale, and although assays on several shales have not indicated any direct relation between the iron content and the gold content, it seems far more reasonable to expect that should gold at any time be found, it would be more liable to be found in the sandstone seams between the layers of shale.

5. With regard to the material identified as lead and zinc, found on the concentrating table in the mill, the Bureau representatives suggest that this material was probably some that had remained in the elevator pits and launders and pump boxes in the old concentrating mill, the latter probably not having been thoroughly cleaned when the mill had been closed down after having been operated as a sampling mill concentrator. The Bureau's representatives do not believe that this material was intentionally added to the shale.

6. A sample of the decarbonized shale was handed Mr. Himes, the owner of the property in Wyoming, from which the samples of shale were taken. He reported he had it assayed in Denver. The Bureau's assays on this material indicated .04 ounce per ton, or 80¢ value in gold. Mr. Himes advised that Mr. Burlingame, commercial assayer in Denver, obtained 85¢ from the same material. He also advised that Mr. A. M. Beam obtained from a portion of the same sample $6 per ton in gold and silver values. --Reports of Investigations, U.S. Bureau of Mines.

METHOD OF TREATMENT FOR DETERMINATION OF OIL YIELD AND PRECIOUS METALS IN OIL SHALES

CRUDE OIL SHALE
(Crushed to pass 1/2 inch)

RETORT ASSAY

RESIDUE

DECARBONIZED SHALE

CRUDE OIL 25 GAL.PER TON

SPECIFIC GRAVITY	S.POINT	UNSAT.	DIST.%
910	31.2	49.2	33.2

SHALE INDEX (2 HR)
4.07

OIL INDEX
16.4

CONCENTRATION TEST ON WILFLEY TABLE

CONCENTRATES TAILS

CHLORINATION TREATMENT

HYDROCHLORIC ACID LEACH
(dilute solution, and wash water)

RESIDUE **SOLUTION**

ASSAY

PRECIPITATE ON C. P. GRANULATED ZINC

FILTER OUT AND PRECIPITATE-ADD FRESH ZINC AND REPEAT AS ABOVE

SOLUTION **PRECIPITATE**

WASH WITH WATER AND DISSOLVE IN HYDROCHLORIDE OR SULPHURIC ACID

SOLUTION **RESIDUE**

WASH, DRY, ADD SILVER - WRAP IN LEAD FOIL, ASSAY.

CYANIDE TREATMENT

25% KCN SOLUTION--RATIO L-S (3-1)

AGITATE SOLUTIONS FOR 24, 48 AND 72 HOURS. FILTERED & WASHED

ASSAYED SOLUTIONS AND RESIDUES