MAR 19680085: MIKKWA RIVER

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ECONOMIC MINERALS FILE REPORT No. S-AF-091(2)

SUPPLEMENT TO PRELIMINARY GEOLOGICAL REPORT SULPHUR PROSPECTING PERMIT MIKKWA RIVER AREA NORTH-CENTRAL ALBERTA /9680085

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Prepared for

A. Andrekson

April, 1968

J. W. Worobec Geological Consultant

October 15, 1968

Eugene T. Hall

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PRELIMINARY GEOLOGICAL REPORT SULPHUR PROSPECTING PERMIT #91

Mikkwa River Area North Central Alberta Prepared for Alexander Andrekson, Edmonton, Alberta

INTRODUCTION

This report has been prepared at the request of Mr. Alexander Andrekson, the present holder of sulphur prospecting permit #91. This permit, covering a total of 99,840 acres, was issued on January 11, 1968. Winter conditions did not permit a preliminary field examination of the properties; therefore, this report covers only that information available from the published and unpublished data.

The property is described as follows:

(A) Township 99 Range 6 West of the Fifth Meridian

Sections 3 to 11, inclusive
 Sections 14 to 23, inclusive
 Sections 26 to 35, inclusive

(B) Township 100 Range 6 West of the Fifth Meridian

1. Sections 1 to 36, inclusive

(C) Township 101 Range 6 West of the Fifth Meridian

1. Sections 1 to 36, inclusive

(D) Township 99 Range 7 West of the Fifth Meridian

1. Section 36

(E) Township 100 Range 7 West of the Fifth Meridian

1. Sections 1, 2, 3

2. Sections 10 to 15, inclusive 3. Sections 22 to 27, inclusive 4. Sections 34 to 36, inclusive

(F) Township 101 Range 7 West of the Fifth Meridian

1. Sections 1 to 36, inclusive

The permit is located approximately 70 miles southeast of the town of Fort Vermilion. The property is readily accessible during the winter months to wheeled drilling equipment via several seismic lines that cross the area and bulldozing new lines where necessary. Summer drilling can be accomplished by tracked equipment by using existing seismic lines; however, the cost of opening new lines during summer months would be prohibitive.

Deposits of elemental sulphur beds have been reported from many localities in northern Alberta and the southern portion of the Northwest Territories as early as 1910. In many instances, these deposits were often found around sulphur water springs and/or gas seeps. Sulphur deposits have also been observed as thin interbeds with shale deposits and infilling of cavities in porous carbonate rocks at a few localities where outcrops are exposed along stream channels.

Very little attention was given to these sulphur occurrences in past because the supply of sulphur exceeded the demand. Price increases and growing world demand for sulphur renewed interest in these deposits. H. L. Hunt and associates, after several months of surface reconnaissance, filed sulphur prospecting permits #8, #9 and #10. Surface samples assayed as high as 95% elemental

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sulphur. This announcement activated a large land play wherein some six million acres in the vicinity of the Hunt permits were filed on. The permittees included many major companies as well as small companies and individuals.

The time element precluded the opportunity of detailed study or surface reconnaissance, and many permits were filed solely on the basis of proximity.

Relation of Regional Geology to the Sulphur Deposits

The geologic process by which the sulphur deposits were emplaced, their frequency of occurrence, the possible extent or size of an individual deposit are as yet unknown. On the basis of what little exploratory work that has been done at this time, the prospects are highly encouraging that this area will eventually be a commercial producer.

Over the past three months, several companies have carried out preliminary shallow drilling programs to take advantage of winter drilling conditions. The results are being held confidential; however, in several instances, additional follow-up drilling is planned for the 1968-69 winter season. At least two tracked drilling units will be located in this area to carry out summer drilling programs.

The sulphur occurs in the amphorous state and in the monoclinic and rhombic crystalline forms. Two hypothesis as to the

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origin of sulphur are currently in use. The first theory suggests that the sulphur deposits are the result of sulphur bearing waters and gases moving up to dip to outcrop or sub-crop edges of the Upper Devonian Grosmont reef and the Middle Devonian Keg River or its equivalent termed the Methy Dolomite. In other instances, fault planes are believed to be the escape route of the waters and gases from the underlying reefs. Several sulphur springs, bubbling water and gas surrounded by elemental sulphur deposits support this theory.

The second possible source of the sulphur is believed to be the decomposition of the vast sulphate deposits of the Middle Devonian Elk Point Group. The chemistry of the decomposition of calcium-magnesium sulphates into elemental sulphur can be accomplished experimentally. In nature, it is assumed that the process involves bacterial action in conjunction with moving subterranean waters and hydrocarbons. The impurities of both magnesium and sulphate in widely varying proportions found with elemental sulphur tend to support this hypothesis.

It is highly likely that future study will demonstrate that both processes contributed to the origin of these sulphur deposits. The presence of magnesium as an impurity could develop into a valuable by-product.

<u>Recommended Evaluation Program</u>

The photogeologic evidence of faulting in the near vicinity and the occurrence sulphur springs nearby, particularly on

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Lambert Creek, indicates the likelihood of finding sulphur deposits on permit #91. The following evaluation program is recommended.

- A photogeologic study of the aerial photographs to locate surface expression of faulting, sulphur springs and possible vegetation kill.
- 2. The possible use of infra-red photography to determine a relationship between thermal activity and sulphur deposition.
- 3. A surface examination to verify data revealed through the air-photo study. A portable augur for shallow holes to test any surface deposits of sulphur.
- 4. A shallow drilling program be initiated, if warranted, to roughly delineate any sulphur deposits found.

Respectfully submitted,

J. W. Worobec Geologist

PROCESSES FOR NATIVE SULPHUR ORES

INTRODUCTION DEMAND FOR SULPHUR FRASCH SULPHUR PRODUCTION RECOVERY OF SULPHUR FROM NATIVE ORES EVALUATION OF PRODUCTION ECONOMICS THE FUTURE OF SULPHUR

INTRODUCTION

Until the birth of the modern chemical industry in the middle of the 18th Century, sulphur had been used through the years as a medicinal substance and in a somewhat more spectacular manner as one of the ingredients of gunpowder. Traditionally the world's supply of the yellow element had been secured by hand sorting at high grade volcanic deposits and, to a lesser extent, by crude refining of lower grade ores. The rising demand for sulphuric acid in the 19th Century caused a boom in the sulphur industry and was responsible for the entry of iron pyrites as a source of sulphuric acid. Subsequently, the production of sulphuric acid from relatively high capital cost pyrite roasting plants has traditionally acted as a check on the world price of sulphur. Although not reviewed in this article, the recovery of elemental sulphur from natural gas and other hydrocarbon sources and from industrial stack gases has steadily risen to become a significant factor in world sulphur production.

DEMAND FOR SULPHUR

The world demand for sulphur is growing at the approximate rate of 7% per annum. This growth in consumption can be attributed to the more intensive use of fertilizers in developing countries and the high level of activity in the chemical industry in developed countries. Approximately 85% of all sulphur produced ends up as sulphuric acid, of which nearly half goes into the production of fertilizer.

In 1967 free world sulphur production rose to a new high of about 26 million tons, of which over half was produced in North and Central America. It has been estimated that free world sulphur reserves amount to over 400 million tons of sulphur, to which should be added some 150 million tons in Communist countries. To date, by far the greatest single source of production is from Frasch sources; however, the currently prevailing market prices, coupled with improved technology, will tend to bring other sources into production at an increased rate in the foreseeable future.

FRASCH SULPHUR PRODUCTION

The Frasch process by which large underground deposits of sulphur can be mined economically is simple in theory, but complex in practice. Given the ideal conditions of a domal structure with a covering of impervious caprock, sulphur is recovered by injecting superheated water to the sulphur bearing horizon and raising the molten sulphur to the surface by means of compressed air.

- 1. Direct Burning
- 2. Distillation
- 3. Autoclaving and Agglomeration

4. Flotation

5. Melting and Filtering

6. Solvent Extraction

Most current research and process development is devoted to improving one or more of these processes.

Direct Burning Processes:

(a) Colcarella Process:

This primitive process consists of piling the ore and burning it freely. The major part of the sulphur burns out and the heat produced melts the balance. Recovery is only in the order of 30%, the product is of poor quality; hence this process has fallen into disuse.

(b) Calcarone and Gill Process:

These processes are used in Italy. They both use heat liberated by burning part of the sulphur in the ore to liquefy and vaporize the remaining sulphur which is recovered by solidification or condensation.

The Calcarone kiln usually consists of a cone 35 feet at the base and some 18 to 20 feet high. A kiln of 25,000 cu. ft. capacity would yield, about 200 tons of sulphur after two months of combustion.

The Gill furnace consists of a series of chambers with domed roofs. Sulphur is burned and melted in the first chamber and the hot combustion gases are used to heat the charge in the subsequent chambers. Combustion in these cells will last between four and eight days.

Minimum grade of ore for feed in both the above systems is 20% sulphur, and the recovery varies between 50% and 60%. Sulphur produced ranges from 95% to 99% purity and does not meet modern commercial requirements.

Distillation:

In the early part of this century a number of distillation plants were in use in Europe. These installations utilized coal fired cast iron retorts to bring the sulphur to the boiling point (447.5^o C.). The sulphur

-- 3'---

vapor produced was collected and cooled in brick lined condensers. A good grade of sulphur was produced, but high fuel consumption (450 pounds coal) per ton of sulphur produced) rendered the process expensive. Attempts to reduce fuel consumption by using rotary retorts did not prove generally satisfactory.

Some distillation plants are in production today in Italy and Japan. These plants, utilizing modern methods of waste heat recovery, apparently produce a good product at a competitive cost.

Autoclaving:

Autoclaving to recover sulphur from ore is widely used in Japan and in some parts of South America. Autoclaves are of either stationary or rotary type. In Chile cast iron stationary autoclaves with a capacity of soone to two tons of feed are common. These are charged with high grade concentrates and steam is injected at 50 to 60 pounds pressure. The sulphur melts away from the gangue and is tapped through a door below a grate supporting the charge. With stationary autoclaves typical operating conditions would be as follows:

> Water 0.7-1.0 tons per ton of sulphur ph 8-----8 Steam pressure 50-60 p. s. i. Steam time 30-40 minutes Grinding -48 mesh Complete cycle time 2 to 2-1/2 hours Grade of feed --- 70% S Sulphur recovery 50% Grade of product 99.0% S

Rotary autoclaves are now proving popular and it is claimed that the added capital cost is offset by reduced steam requirements and a higher purity product. One process involving autoclaving in a coiled tube type of autoclave apparently shows promise.

Agglomeration:

An agglomeration process was developed in Chile in 1942 and has been used with some success. In this process a 75% flotation concentrate is heated to its melting point in an autoclave. Sulphuric acid is added to wet the gangue and the sulphur collects in the bottom of the vessel. The gangue agglomerates and is filtered from the sulphur. Acid used is in the order of 240 pounds per ton of sulphur.

Both the autoclaving and agglomeration processes possess the inherent disadvantages of batch operation and, consequently, production costs are relatively high.

Flotation;

Sulphur is readily amenable to separation from its ore by flotation utilizing hydrocarbons as reagents. A two or three stage cleaning circuit can give a 90% grade of concentrate with an 85% recovery of the originally contained sulphur. Further processing by autoclaving or melting and filtering is normally required to remove finely occluded gangue particles and thus to improve marketability. Flotation, being a continuous process, lends itself to high tonnage operations and promises good possibilities of economic recovery of native sulphur. Commercial flotation plants are in operation in many areas of the world, including Sicily. Italy and Latin America, and treat ores ranging in sulphur content upwards from 20%.

Solvent Extraction:

Sulphur will dissolve in a variety of solvents, usually best at the melting point (246° F.). The principal solvents in commercial use are carbon disulfide, carbon tetrachloride, benzine and some of the aromatic petroleum solvents. Some salts such as calcium magnesium and zinc chloride have been used as solvents; however, with these, there is an appreciable loss of salt in the residue and the product is of relatively low quality. With organic solvents, a grade of 99.7% sulphur can be achieved at very high recovery rate (98.5%).

The main steps in the solvent extraction process are fine grinding, mixing with solvent at a temperature of approximately 250° F., gangue separation, recovery of solvent from gangue, solvent distillation and sulphur purification. Some solvents present hazards of toxicity and fiammability, and in general the process requires especially developed equipment and expert care in its manipulation. This process has the advantage of continuous operation and should undoubtedly be considered in any process assessment for new plants.

New Plant Design:

When determining the process to use for the recovery of sulphur from a native deposit not suited to Frasch mining, the most economical process will likely be a combination of two or more of those described in the foregoing. Each process must be studied on its own merits and, in most instances, laboratory and pilot plant work will be required before process design and capital and operating costs can be accurately determined.

EVALUATION OF PRODUCTION ECONOMICS

In arriving at the decision of whether and how to bring a given deposit into production, a number of important factors must be clearly identified and their significance assessed in economic terms. A proper feasibility study is essential to document fully the following important aspects of a project as an aid to decision making:

-Sponsor's objectives

-Nature and scope of the project.

-Definition of feasible alternatives

-Process selection and preparation of preliminary flow sheets and design

-Estimates of capital investment and operating costs, transportation costs, revenues and rates of return

-Sensitivity analysis of rate of return to key variables

-Assessment of technical, financial and other risks associated with the project

-Outline of additional development work between major capital authorizations

Sponsor's Objectives. All too often these are left unquestioned and based on untested assumptions-unless clearly spelled out, the various parties involved in launching a project can easily be working at odds.

Nature and Scope of the Project: A full and thorough documentation of this aspect will force consideration of the physical, technical, tenancial and economic limitations of the project being considered.

Feasible Alternatives. A general assessment may be all that is required to narrow down alternatives which are technically feasible to a few for more detailed consideration in order to select the best process combination and scale of operation.

Estimates of Capital and Operating Cost and Measures of Profitability: Great care must be taken to ensure that all major items of cost chargeable to the project are foreseen and estimated. In order to project realistic cash flows, due consideration must be given to the effect of income taxes, capital cost allowances, depletion, depreciation, royalties and taxes. start-up costs, working capital requirements, marketing and transportation costs, and any items of cost which would not otherwise be incurred if the project were not initiated. In this stage ranges of probability for the major items of cost should be bracketed and detailed cash flows and measures of profitability (discounted cash flow rate of return) prepared for each alternative identified; graphs should be prepared showing the variation in rate of return as each major item is charged over its probable range. Such analysis, commonly called a sensitivity analysis, is an invaluable management tool which can be used to assess the financial and economic risks associated with a project. The major items that normally require sensitivity analysis are:

-selling price

-level of production

-reserves

-scope of operation

-capital cost

-key operating costs, i.e. as reflected from water rate in a Frasch operation

It is apparent that this analytical technique becomes onerous to apply manually and a computer is an invaluable aid to such computations. The readily available use of computers to anyone at modest cost today is a boon to such decision-making tools. Exhibit 1 attached shows a simplified example of a sensitivity analysis calculated for a Frasch operation.

Financing Charges: One of the most common fallacies prevalent in economic evaluations today is the inclusion of interest. (inancing charges and certain other capital charges in the projection of cash flows for purposes of the economic evaluation of a project. When this procedure is followed, the true economic merit of the project itself is seldom discovered and the resultant comparisons of alternatives are distorted. Only after the most economic alternative has been selected, and rate of return criteria have been assessed, based on the true economic merit of the project, should financing costs, ownership costs, interest and the like be superimposed on the resulting cash flow series to determine the project's ability to support a contemplated capital structure.

Additional Development Work: On the basis of a thorough assessment of risks, the need and justification for additional development work, to produce more detailed information, often becomes apparent. If such is not the case, and if profitability criteria have been met, management has documented before it the basis for effective decision-making and may then authorize detailed design, contract negotiations, financing arrangements and firm planning for the commissioning of the project.

THE FUTURE OF SULPHUR

The sulphur industry appears to be one which possesses good prospects for long term stability. The effect of alternate methods of fertilizer and sulphuric acid production will undoubtedly continue to discourage excessive price fluctuations for brimstone, but on the other hand, a steadily increasing demand, coupled with the development of new processes will aid in placing low grade and remote ore sources into production. Provided the basic precepts of modern management are followed, the operator considering an entry into the sulphur field should have excellent prospects for financial success.

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February 13, 1968



THE DUBOW TECHNIQUE

The Dubow Technique is applicable to the extraction of elemental sulphur from almost any ore. The free sulphur deposits, which have been found in north-central Alberta, appear to be ideally suited to use of this technique. Dubow Chemical Corporation reserves a 5% royalty of product in kind from every installation producing by its technique.

The Joseph L. Prosser & Co. of Glenarm, Maryland, has had previous experience in turnkeying the design of a plant, supervision of construction and placing it on stream with a warranty of production of 99.6% sulphur in liquid or dry state in a quantity predicated on feed-stock grade. The higher the sulphur content, the lower the extraction cost. 99.6% pure molten sulphur is produced for a cost bearing from \$8.00 to \$16.00 per net ton consistent on grade and feed-stock, labor and mining cost, proximity to water, power and fuel.

Although the present domestic price of sulphur in the United States is \$39.00 per ton, and Canadian prices are relatively comparable, only old contracts are filled at this price. New contracts are being made for prices which have been considerably higher and this condition should persist for at least another five years, based on present circumstance. Current conditions will probably cause the price of sulphur to stabilize at \$50.00.

Current production is from the Frasch Process since present known means of extracting deposits are not economical. However, with the Dubow Technique this situation is changed and an opportunity is available to exploit previously uneconomical sulphur deposits. Estimated costs of plant construction, etc., are available through the office of Parkman Petroleums Limited.

COST OF PLANT AND FACILITIES

Plant	\$1500000.00
Water to installation	50000.00
Power	25000.00
Road	225000.00
Camp site	100000.00
	\$190000.00
Working capital	60000.00
Total investment	\$250000.00

PRODUCTION COST PER TON

Utilities and chemicals	\$	6.50
Labor, supervision, maintenance	•	1 10
Taxes, insurance, overhead interest		1 00
Depreciation		1.20
		.45
Mining, atc.		3.00
iotal extraction cost	\$	12.25

TYPICAL PLANT

Capacity-750 TPD

Annual operating time-330 days

CONSTRUCTION COST

Ore storage and grinding Equipment

\$ 250000.00

C J D T Piller P		
Dre feeder	\$ 8000.00	
Ore heater & accessories	3 6500 .00	
Ore storage-ground	12000.00	
Mixer tanks w/mixer, coils	11000.00	
Thickener tank w/mechanism	20000.00	
Wash tank	5500.00	
Wash separator tank	19000.00	
Pump tanks	500 0. 00	
Solvent heater	16000.00	
Solvent cooler	21500.00	
Sulphur melter	6000.00	
Occluded sulphur tank	5000.00	
Melt tank	4000.00	
Pumps-12	18000.00	
Boiler	40000.00	
Sub-total		222500.00
Building-60X120 @ \$4.00/sq. ft.		28800.00
Electrical-1500 HP @ \$40.00/HP		60000.00
Lighting and miscellaneous		8200.00
Instruments		25000.00
Earthwork and foundations		8000.00
Piping		40000 . 0 0
Insulation		2000.00
Molten sulphur storage		25000.00
Installation, field, freight		142500.00
Engineering		55000.00
Contractor O. H. & P.		125000.00
Grand total		\$1235000.00

PRODUCTION COST

÷

Utilities		
Power- 50 KWH∕T @ 1¢ \$.50		
Fuel- 1.5MM BTU/T @ 50¢ .75		
Solvent- 40 G/T @ 10½¢ 4.10		
Pine oil- 5 #/T @ 12¢ .60		
Wetting agent- 10 $\#/T @ 5¢$.50		
Sub-total	\$	6.45
Direct cost		
Labor- 4 men/shift, 4 shifts \$116500.00		
Supervisors- 4 48000.00		
Maintenance- 8% of investment 98800.00		_
Subtotal		1.10
Indirect cost	۱	
Taxes, insurance- 3% \$ 37000.00		
Plant, office overhead 200000.00		
Interest on investment- 7% 113200.00		
Sub-total		1.40
Depreciation		.50
Mining and into plant		3.00
Cost of sulphur/T without any royalty provision	5	12.45
For 1000TPD plant increased size of components		
will raise the total construction cost to	\$14650	00,00
r - 1000100 -lost production onet reduced to	ч£	11.95
FOR THOMES DIALS, DIRACTION COSC LENGER OF	Ψ	/

TECHNOLOGY

sulphur

comparable price for the product in the country of export. There must also be proof of actual injury or real threat of injury to a domestic industry. The principle is sound, but actual practice may present some problems.

The machinery item is the most significant and also the most complex ever put into effect, from Jan. 1. There is no class or kind qualification. The primary rate will be 15 percent MFN and 2½ percent British Preference. Department officials have estimated that importers will be able to cut their machinery costs by \$45 million a year by importing machinery not available from production in Canada free of duty. We recommend that this item is important enough to have senior management attention.

Effective communications, by Robert L. Switzer, Atlantic Richfield Company, Dallas.

The perfection of communications is a never-ending quest. Effective writing is an important feature of it, but even PhD's cannot all express themselves in writing.

Problems in the field of communications are mostly people and their personal communications, more often than mechanical and technical expressions.

We have some of the most ingenious communications media ever known. We are on the threshold of even more dramatic items. But still the major problem of dealing with people around us results in less than optimum use of these elaborate facilities.

Nearly everything starts with a better idea, but it has to be developed and sold to management before it can be put into operation. The ability to express and sell the idea is the key to its survival.

How sulphur deposits are formed in Northern Alta.

By Edward Lewis Jones, Consulting Engineer, Calgary

Sulphur deposits at the surface in northern Alberta have attracted a lot of attention in recent months. The method by which the sulphur is deposited is of considerable interest since the sulphur itself is quite pure, and suitable for the manufacture of sulphuric acid, being free of arsenic, selenium and tellurium, the catalyst poisons.

The surface deposits, however, are mixed with sand and silt, which could indicate that the sulphur was being deposited while the wind was blowing in the gangue material from elsewhere. Even so, the deposits are quite high in percentage of sulphur.

While there are several theories on the formation of sulphur deposits, the writer prefers the geochemical theory outlined below, rather than the others discussed first:

Volcanic sulphur

The existence of sulphur from volcanic fissures is known, but many deposits of volcanic origin contain the catalyst poisons mentioned above, thereby disqualifying them from producing marketable sulphur. Volcanic sulphur, like that from sour natural gas, may be deposited by burning hydrogen sulphide.

Geo-bacterial reducation of sulphate

Several kinds of bacteria can reduce sulphate to sulphur. Much comparison of isotope ratios in sulphur



Associated Helicopters took advantage of CFCN Calgary's newly licensed heliport to introduce families of their clients in the oil and mining industries to the Bell 204 turbine helicopter. Rides kept the crew busy for two days.

has lent credence to the theory that bacteria formed the large sulphur deposits in the salt domes near the Gulf of Mexico. But no rates of deposition or material balances have been made, particularly relating the ratio of the remains of the bacteria to the sulphur deposited. Geo-bacterial reduction is very slow, particularly in cold climates like Canada's. British Petroleum in Libya has not produced substantial quantities of sulphur from bacterial reduction of sulphate, even in a hot climate.

Inorganic reduction of sulphate

Chemical equations showing the formation of sulphur from sulphate minerals, such as anhydrate, generally require far too drastic conditions of temperature to be given serious consideration in a natural environment. One example is the reduction of calcium sulphate with carbon, generally practiced in England. Even there, sulphur dioxide is the main product from which sulphuric acid is made, not sulphur, the marketable product, in demand since it is shipped most economically.

However, elemental sulphur is always found in association with carbonate and sulphate, complete with sulphurous water containing hydrogen sulphide. Usually salt is nearby also, creating differential voltages between salt solutions.

Geochemical theory

Once the assumption has been made that water containing ions of sulphate minerals and hydrogen sulphide is exposed to small electro chemical voltages, possibly generated through fractures and contacts with underlying salt beds, certain equilibria relating to mineral solutions may be used to define the conditions under which native sulphur could be deposited in natural environments.

Recent developments in computing mineral stability diagrams explain how native sulphur deposits can develop.

In an environment of water carrying sulphate and hydrogen sulphide at 60 F and atmospheric pressure, elemental sulphur can be formed under certain conditions of low electro chemical voltage and low pH. C. Valensi (Contribution au diagramme potential-pH du soufre, Comp. rendu, 2eme Reunion) shows that the naturally occurring ionic species, which are stable, are sulphate ion, bisulphate, hydrogen sulphide, bisulphide ion, sulphide ion, and native sulphur.

The electrochemical voltage is measured against a background of salt (which is usually found associated in nature), and is commonly termed the half-cell voltage, and labelled E_{h} .

A plot of E_h against the pH, which measures the acidity or alkalinity of the water solution (7.0 pH being neutral), defines the borders between which the several ions exist, including native sulphur.

Where the solution is acid, hydrogen sulphide exists in the low pH range. As the solution becomes more alkaline, HS- and S-- are formed:

The equilibrium between the species is one when pH = 7. Similarly,

^KHS- =
$$(H^+)(S^{--})$$
 or
 (HS^-) or
 $(S^{--}) = KHS^- = 10^{-14}$
 $(HS^-) = (HS^-)^{-14}$

and (S--) = (HS-) when pH = 14, so the boundaries between the species are vertical lines on the diagram at pH7 (Line 1) and pH14 (Line 2) regardless of electrochemical voltage.

However, oxidation of sulphurcontaining ions will be as follows:

$$H_2S_{aq}$$
. + 4 H_2O gives
HSO₄- + 9H+ + 8e



LINES OF EQUAL IONIC CONCENTRATIONS OF SULPHUR IONS IN WATER SOLUTIONS AT 60°F.

From the free-energy equation the electrochemical voltage may be determined in terms of pH and ionic concentrations. The boundaries between sulphur species at equal concentrations occur when the ionic ratio is one, leaving only equations in terms of E_h and pH which may be plotted on the diagram too.

Line 3
$$E_h = 0.290 - 0.066 \text{ pH} +$$

0.0074 $\log \frac{(\text{HSO}_4-)}{(\text{H}_2\text{S})} =$

0.290 - 0.066 pH.

Similarly, Line 4 for the boundary between SO_4 = & H₂S is E_h = 0.30 - 0.073 pH,

and Line 5 for the boundary between SO_4 = & HS- is E_h = 0.25 - 0.067 pH

and the boundary between (HSO_4-) and $(H+) + (SO_4=)$

$$\frac{(SO_4)}{(HSO_4)} = \frac{KHSO_4^{-}}{(H^+)} = \frac{10^{-1.9}}{(H^+)}$$

is line six at a pH of 1.9. See Figure 1.

The diagram shows the boundaries of equal concentrations of the ions, independently of the total dissolved sulphur.

Crystalline (yellow) sulphur precipitates

Where the total dissolved sulphur has an activity corresponding to 10^{-1} , similar to that of hydrogen sulphide in water at 60° F., the activity of the sulphide ion may be shown to be

$$H_2S_{aq} = S = {}_{aq} + 2H^+$$
 and
 $\frac{(S=)(H^+)^2}{(H_2S)} = K = 10^{-21}$
or log $S= -22 + 2pH$.

Similarly boundaries between crystalline sulphur with an activity of one, and the other sulphur ions may be computed, and are shown on the diagram in Figure 2, for a total sulphur of 10^{-1} , from the equations

$$H_{2}S_{aq} = \text{solid } S + 2H^{+}_{aq} + 2e$$

$$HS_{aq} = \text{solid } S + H^{+}_{aq} + 2e$$

$$S = - = \text{solid } S + 2e$$

Solid S +
$$4H_2O$$
 =
HSO = + $7H^+$ or + $6e$



CONDITIONS FOR DEPOSITS OF NATIVE TO FORM FROM WATER SOLUTIONS OF SULPHATE 1. SOME ELECTROCHEMICAL VOLTAGE IN NEUTRAL SOLUTIONS AND;

2. NO VOLTAGE DIFFERENCES IN ACID SOLUTIONS

Practical application

The theory shows that elemental sulphur may form enormous deposits from solutions, as apparently has occurred in the surface deposits of sulphur in the Northwest Territories and northern Alberta.

The voltage differences are small, and within that range expected in the field from ionic solutions in springs or in faulted areas, or downhole in wells.

Where the pH is low, i.e., where hydrogen sulphide gas is present, solid sulphur is deposited faster, even at minimal voltage differences.

Other sulphides such as pyrite can form sulphur from water solution. Similar diagrams may be prepared for sulphur deposition from pyrite. This may account for some sulphur formations in northern Alberta, where iron compounds are found mixed with sulphur.

The E_h —pH diagrams can be used to show the stability of sulphur relative to other minerals in water solution.

The high purity of surface sulphur deposits, i.e., freedom from catalyst poisons like arsenic, is explained.

The pH range of waters in the Northwest Territories falls within that required for sulphur deposition.

Particularly since the sulphate is more soluble in cold water than hot, a possible process for recovering sulphur from calcium sulphate is evident, although the economics are indefinite.

Reference — M. J. Pourbaix, Thermodynamics of Dilute Aqueous Solutions, 1949.



			-		TCC	UE D	HOLDER	DOPES
DER	ACRES	NO.		K 1	100	1 60	Tobo Minor	10 5.82
co Expl.	39,680	127.	116	2 0	30-	1-68	Nugent Sales	19.840
ern Decalta	99.840	129.	107	4 5	30-	1-68	C.E. Dolan	5,120
1 Canada	99,520	130.	107	11 5	30-	1-68	Abtec Equip.	19,840
1 Canada	97,230	131.	113	4 5	30-	1-68	H.P. Killoran	19,840
hillips	59,520	132.	101	3 5	30-	1-68	J.F. Grimm	99,840
sant-W'dwide	38,400	134.	101	5 5	5 30-	1-68	A.G. Hatsis	59,520
Pearce	19,840	135.	116	3 5	5 30-	1-68	Bata Resources	19,840
c	19,840	136.	113	7	5 30-	1-68	Bata Resources	19,840
ons Drlg.	38,400	137.	120	1 1	5 30-	1-68	Montclair .	19,840
IC	47.360	139.	125	11 :	5 30-	1-68	Montclair	19,840
alta-Fisher	19,840	140.	126	10 :	5 30-	1-68	Montclair	19,840
0.G.	99,840	141.	125	10 1	5 30-	1-68	Montclair	19,840
011 Land	19,840	142.	113	4	5 30-	1-68	H.P. Killoran	19,840
ll Canada	99,840	144.	108	11	5 7-	2-68	Western Land	19,576
Ll Canada	98,560	145.	101	3 !	5 7-	2-68	J. Superstein	39,680
Star Petr.	19,840	146.	114	3	5 7-	2-68	Alexandra Petr.	19,840
ed Mineral	19.840	148.	119	1	5 7-	2-68	D.A. Campbell	19,840
ence Oil	19,840	149.	98	11	5 7-	2-68	H.P. Killoran	19,840
ence Oil	19,840	150.	112	13	5 7-	2-68	R. Superstein	19,840
ence Oil	19,840	151.	109	14	5 7-	2-68	R. Superstein	19,840
ence Oil	19,840	153.	108	12	5 7-	2-68	Milo Building	39,680
an dreks on	99,840	154.	113	8	5 7-	2-68	Milo Building	39,680
ada-Cdn Sup	59,885	155.	99	5	5 7-	2-68	Milo Building	39,680
ka-Canadian	33,280	150.	101	12	5 8-	2-68	Ranger Oil	19,840
ka-Canadian	39,680	158.	89	5	4 8-	2-68	H.L. Banting	19,840
pil	80,000	159.	105	11	5 12-	2-68	Abidonne Oils	19,840
Petr.	19,840	160.	94	1	5 12-	2-68	Abidonne Oils	19,840
Petr.	19 940	161.	115	17	L 12-	2-68	Imperial Oil Ent	99.840
lair Canada	19,840	163.	104	13	5 12-	2-68	Abidonne Oils	19,840
lair Canada	19,840	, 16 4.	113	5	5 12-	2-68	Abidonne Oils	19,840
lair Canada	19,840	165.	117	5	5 16-	2-68	Peyto Oils Buffalo Minoral	19,840
lair Canada	11,520	167.	114	4	5 16-	2-68	Heritage Hold.	39,680
ohnston	39,680	168.	100	9	4 21-	2-68	G.W. Goettler	59,520
reland Power	19,840	169.	116	7	5 21-	2-68	Peyto Oils	19,840
tage Hold.	39,040	170.	120	2	5 21-	2-68	D.A. Campbell	19,840
Tappour	39,680	171.	98	13	5 21-	-2-68	Amerada	19,840
ional Trust	18,560	173.	117	10	5 21-	2-68	Farmers Chem.	19.840
. Superior	99,840	174.	116	7	5 21-	2-68	Farmers Chem.	19,840
. Kirwan	3,840	175.	107	15	5 21-	2-68	D.L. Hope	19,840
Bonanza	19,840	176.	119	1	5 26-	2-68	R. Thomas	8,320
ional Petr.	39,680	177.	101	18	5 26-	2-68	Aztec Oil & Gas	19,840
Lake Mines	19,840	179.	101	12	5 27-	2-68	G. Lonn	19,840
11 Lake Mines	19,840	180.	106	13	5 27-	2-6.8	G. Lonn	19,840
LI Lake Mines	19,840	181.	116	11	5 5-	3-68	Syracuse	19,840
11 Lake Mines	19,840	182.	106	13	5 21-	3-68	Arco	39,680
Ll Lake Mines	19,840	184.	89	3	4 29-	3-68	Sinclair	39,840
Ll Lake Mines	19,840	185.	96	2	4 29-	3-68	Sinclair	37,280
ll Lake Mines	19,840	186.	97	4	4 29-	3-68	Sinclair	36.334
11 Lake Mines	19,840	188	88	8	4 29-	3-68	Sinclair	39,840
. Tannous	19.840	189.	90	9	4 29-	3-68	Sinclair	73,069
	UB	190.	97	. 10	4 29-	3-68	Sinclair	99,137
4 3	2 0	192	102	10	4 29-	3-68	Sinclair	98,906
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		103 102 101 100 99 98			TOTAL .	ACREAG	E [.] - 6,845,952	
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Eigure 2- Reproduction of Topographical Sheet Wadlin, Atta

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<u>Figure</u> 2- Reproduction of Topographical Sheet Wadlin, Atta

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DEPARTMENT OF LANDS AND FORESTS

Map Sheet 84 G/B

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Sulphur Springs Lambert Creek





SULPHUR PROSPECTING PERMIT No. 91

