# MAR 19680139: NORTHERN ALBERTA

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## PRELIMINARY STUDY

of

# NORTHERN ALBERTA SULPHUR PERMITS

No. 166 BUFFALO MINERALS LIMITED, Approx. Twp. 116 R 6 w 5th;

Nos. 173 & 174 FARMERS' CHEMICAL LTD., Twps. 116 & 117 R 7 W 5th;

SHOWN ON THE ANNOTATED AIR PHOTO MOSAIC FRONTISPIECES

Geology by

Albert Golden, P.G.cl.

July 23, 1968

Engineering by Edward Lewis Jones, P.Eng.

July 23, 1968

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INDEXING DOCUMENT NO. 200553

# ANNOTATED AIR PHOTO FRONTISPIECE

Sulphur permit areas shown on the air photo mosaic are well located with regard to sulphur deposits, being northwest of the Madison No. 8 discovery and showing similarities on air photos to other sulphur deposits.

The light areas on the air mosaic, marked S, signify characteristic areas where surface sulphur may occur.

Sulphur in low concentrations fertilizes vegetation; but in high concentrations inhibits growth due to the formation of too much acid. The absence of vegetation is another clue to surface sulphur.

These permit areas are surrounded by an outcrop edge of the Lower Cretaceous, which is exposed as small cliffs. Similar cliffs on Madison Permit No. 9 contain beds of sulphur in the cliffs themselves.

Surface deposits of sulphur may be expected in the areas marked on the perimeter of the Lower Cretaceous outcrops.

Subsurface, the contact between the underlying Devonian formations and the Lower Cretaceous under these permits may be the location of subsurface sulphur deposits suitable for Frasch mining. In a similar environment in Pecos County, West Texas, the surface sulphur ore proved to be the surface expression of subsurface deposits which are now being mined by Frasch's method of melting the sulphur underground with hot water.

# GEOLOGICAL BACKGROUND OF SULPHUR IN NORTHERN ALBERTA

Geochemical theory predicts the deposition of sulphur from solutions containing sulphates and hydrogen sulphide. See the attached articles by Pirson and Jones. The Devonian formations contain both hydrogen sulphide and sulphates (i.e., gypsum and anhydrite).

The formations in Alberta which produce sour gas containing hydrogen sulphide occur in the Devonian and the Mississippian.

A wide arc of Devonian exists south from Great Slave Lake on the west side of the Wood Buffalo National Park in Alberta. The thickness of the Middle Devonian beneath these five permits is said to exceed 1,100 feet. Surface sulphur accumulations in Northern Alberta have been known and mentioned by frequent geological surveys in the first part of this century. The local Indians of that area are said to have known of the yellow deposits, and of some which appear like light brown clay.

Surface deposits of sulphur occur in a wide belt from Great Bear Lake, N.W.T. to the Clearwater River in Northern Alberta. These surface deposits are the result of highly sulphurous aqueous solutions which probably arise from underground springs, fault fissures and fracture patterns. The constant discharge of rich-sulphur-bearing solutions from below has resulted in the precipitation of thick accumulations of sulphur bearing rocks, in certain areas. These surface deposits are often very pure, in some instances up to 98% sulphur, and also are associated with limonite, sand, silt and limestones, and gypsum.

The source of the sulphur bearing solutions, which results in surface deposition of this element, are issuing from the truncated Upper Devonian, Woodbend Group which is exposed to the surface (see cross-section \$1) or to the pre-Cretaceous unconformity (see map #1). The staking of sulphur permits has taken place primarily along the wide band of Woodbend subcrop; in areas where the Woodbend is exposed to the surface or where it is masked by Cretaceous erosional remnants.

The deposition of primary elemental sulphur can occur from the aqueous solution of sulphides and sulphates; according to the mineral solution equilibria. Thus, hydrogen sulphide coming from the Devonian formations dissolves in water and reacts with anhydrite and or Gypsum, depositing sulphur out of solution. Since calcium sulphate and hydrogen sulphide are more soluble in cold water than in hot, it could mean a high concentration of sulphur precipitation in areas of Karst topography where surface waters have been extremely Therefore two ingredients are needed for the formation of active. sulphur deposits (1) the presence of sulphates and sulphides, which could have come from iron pyrite concretions, gypsum or anhydrite. (2) The presence of intense water activity which generally occurs at unconformities and results in subterra.nan caverns and sink hole type topography.

Iron pyrite concretions are abundant in the Cretaceous, Cariboo Mountains: and the Woodbend group is known to contain thick beds of anhydrite in the subsurface. The area of study thus appears to have the necessary sulphates and sulphides for a chemical reaction. The needed water to bring about the solution and the later precipitation of sulphur, is evident by the amount of pre-Cretaceous and recent erosion in the area. The evidence of erosional action can be seen by

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digate.

the huge Cretaceous remnants and karst topography in the area. The generally peneplained pre-Cretaceous unconformity indicates a long geologic period of erosion and exposure to surface waters. The present day erosional surface, which incises the peneplained pre-Cretaceous surface, is still vigourously invaded by surface solutions.

The east limb of the Cretaceous, Cariboo Mountains intersects the permits here described, leaving at least half the permits or exposed Woodbend outcrop. The remainder of the permit lies on the Cretaceous Cariboo Mountains. The possibility of concentrated beds of sulphur below the Cretaceous; deposited prior to Cretaceous deposition, during the pre-Cretaceous time of erosion; as well as the present day deposition of sulphur on the exposed Woodbend subcrop is possible on these permits. The presence of sulphur on too of the Cretaceous mountains is also possible due to the presence of iron sulphides in the Cretaceous beds and the movement of subsurface waters from the anhydrite rich Woodbend formation, (see cross-section #1).

The geological formation in which sulphur occurs in the Woodbend (Upper Devonian) Group, is the Grosmont Formation. This formation consists of vuggy, petroliferous, reefoid dolomites, with varying amounts of thin bedded argillaceous limestones. The Grosmont is a -barrier-reef, equivalent in time to the Leduc. In the off-reef facies the Grosmont is equivalent to the Hay River limestones; in the back-reef

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and a later from A .... W E SULPHUR AT PRE. CRETATOSS. SURFACE SULPHUR SURFACE SURFACE - SURFACE SULPHUR 0 PRE CRETACEOUS UNCONFORMITY UISKU SUPPACE HAY RIVER AND HONDO FORMATIONS V IIIIII ¥ 0 GROSMONT, HAY MIKKWA (BEAVERHILL LAKE) UPPER DEVONIAN MUSKEG, KEG RIVER AND CHINCHAGA FORMATIONS 111111\*111 MIDDLE DEVONIAN 17/1 NOTE: 1. SULPHUR AT PRE. CRETACEOUS UNCONFORMITY REPRESENTS OLDER PRE- CRETACEOUS DEPOSITION OF SULPHUR AT UNCONFORMITY. 2. SULPHUR ON TOP OF CRETACEOUS REPRESENTS YOUNGER GENERATION OF EROSION AND SULPHUR DEPOSITION. 3. SULPHUR ON SUBCROP OF WOODBEND. COULD BE PRE- CRETACEOUS OR YOUNGER IN AGE, OR A COMBINATION OF BOTH. THE SULPHUR DEPOSITS IN ALL THREE LOCALS ARE PROGABLY THE RESULT OF SURFACE WATERS, BRINGING TO THE SURFACE AQUEOUS SOLUTIONS OF SULPHIDES AND. SULPHATES LEGEND FROM UNDERLYING BEDS. O IRON SULPHIDE NODULES TITT EVAPORITES (ANHYORITE, DOLONITE AND SALT) SULPHUR DIAGRAMATIC EAST-WEST CROSS SECTION THROUGH 11 FISSURES. FAULTS PROVIDING CHANNEL MAYS 15 FOR MOVEMENT OF SURFACE WATERS. CARIBOO MOUNTAINS MAJOR UNCONFORMITY NO EXACT HORIZONTAL OR. VERTICAL SCALE. TRACES OF KNOWN SULPHUR IN ROCKS .-兴 CROSS SECTION #1. 1968

areas thick evaporite sections (anhydrite) are known as the Hondo Formation. Native sulphur accurrences are known in the Grosmont, Windfall, Sundance, and Nevis, Leduc reefs. The Cretaceous Loon River shales overlie the unconformable Woodbend strata and contain abundant brown ironstone concretions, containing iron sulphide. The Woodbend is underlain by the Mikkwa Formation, which is equivalent to the Beaverhill Lake Formation, in Central Alberta. The Mikkwa Formation is composed primarily of dense, mottled, brown, limestones. Below the Mikkwa the Middle Devonian Muskeg, Keg River and Chinchaga formations are present. The entire Middle Devonian is composed of dolomite, anhydrite and salt. Salt water recoveries in drill-stem tests indicate high sali nities and hydrogen sulphide.

The C osmont and e uivalent formations are exposed along river and creck valleys, certain lake shores and solution sink holes. It is here that native sulphur occurs at the surface as infill in large yugs and in thin beds covering relatively large areas. At Great Slave lake small lenticular pods of sulphur have been observed in Devonian rocks to the east of the study area, thin beds of sulphur have been observed by Norris on the Peace River, in Middle Devonian strata.

The vuggy nature of the Grosmont, the presence of gypsum and anhydrite in equivalent rocks, the ubiquitous occurrence of iron sulphides, the numerous rivers, creeks and sinkholes exposing the Grosmont

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may account for a thick highly concentrated deposit of sulphur in the study area. The possibility of sulphur concentrations at the pre-Cretaceous unconformity and on top of the Cretaceous could also be of considerable value. The concentration of large deposits of sulphur could have occurred before Cretaceous deposition, at the pre-Cretaceous unconformity. These deposits could have been sealed by the impervious Loon River shales. Since sulphur, once precipitated out, is not very soluble in water these deposits would not be susceptible to present day surface water. Faults and fissures from the Woodbend and Cretaceous could be responsible for sulphur accumulations observed on top of Cretaceous rocks.

Example: At Senlac, Saskatchewan, west of Unity, there is a saturated salt spring. The water, saturated with salt, could only have come from the thick salt deposits 3,200 fee below.

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## SULPHUR-BEARING FORMATIONS PRESENT

Practically all the sulphur recovered from sour gas in Alberta originates from the Paleozoic-Mississippian and Devonian systems.

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Although in the subject area the Grosmont is the underlying formation and contains native sulphur, older Devonian formations such as the Beaverhill (Mikkwa) which underlie the northeastern portion of Alberta may also contain sulphur. Subsequently, younger Devonian and Mississippian formations (Winterburn, Wabamun, Banff, etc.) which subcrop successively as one proceeds west from the subject area, may also contain sulphur in situ. This is evident by the occurrence of sulphur at Great Slave Lake which is found in the Devonian Sulphur Point Formation (underlying the Beaverhill) and elsewhere in the Province, at depth.

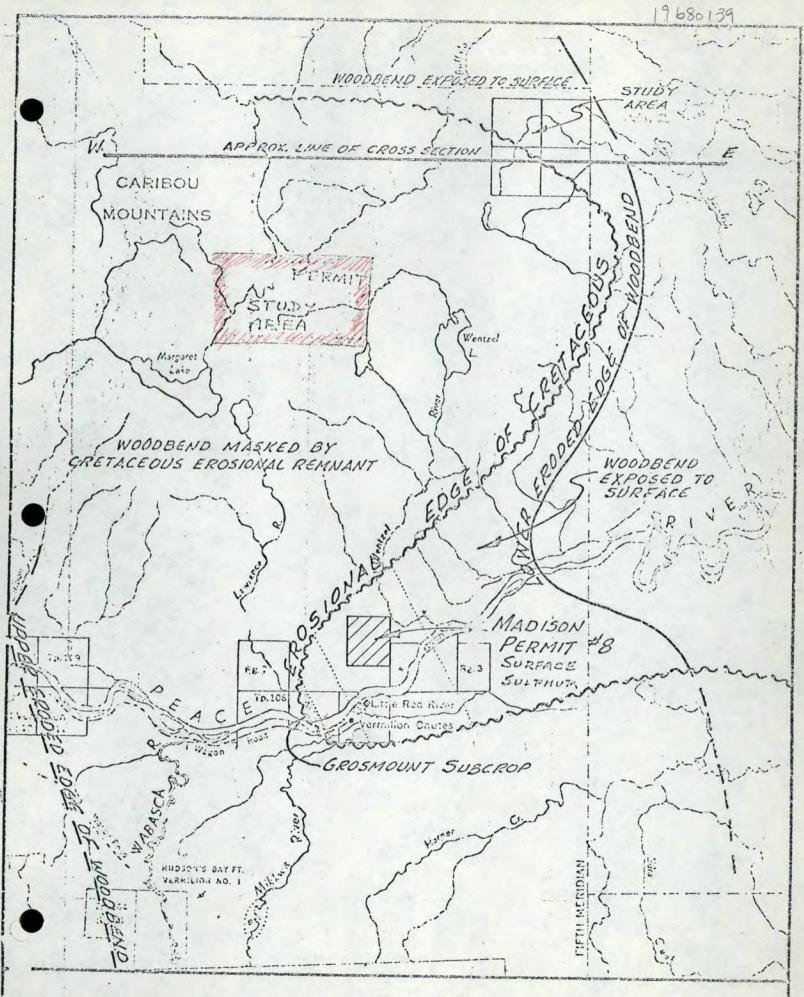
The large Elk Point Salt Basin which parallels an area lying south of the Caribou Mountains, may have on its north flanks, thin salt sections. These salt sections by solution collapse may cause certain subsurface features favoring sulphur accumulation and deposition. Further detailed research and intensive studies of air photo mosaics may indicate certain patterns and alignments of surface features favoring sulphur deposition.

# GEOLOGICAL MAP

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The map shows the Upper and lower erosional edges of the Woodbend formation with the marked Grosmont outcrop along the Peace River, at Vermillion Chutes. The erosional edge of the Cretaceous, where it overlies the Woodbend is also shown.

It is of interest that the subject area lies off the flank of the Cretaceous escarpment and on the exposed Woodbend outcrop. Madison's Permit #8 has a similar geologic position as that of the study area, (see map).  $L_{p} \cdot \#_{1}$ 



MAP #1

#### ENGINEERING

#### 1. Transportation

The locations of the five sulphur permits northwest of Margaret Lake are shown on the attached map of permits.

Rail and road transportation exists along the route of the Mackenzie Highway. There is also a road running from Hilevel to Fort Smith and there are seismic roads on the township lines crossing the five permits.

Barge transportation is possible up the Peace River which is navigable to points crossing the PGE Railroad and the Great Slave Railroad. Moreover, west of Vermilion Falls, south of these five permits, barge transportation is feasible in the summer.

Another possibility is a sulphur slurry pipeline which would be similar to that proposed by Shell Canada Limited to move sulphur to the Pacific.

#### ENCINEERING

2. Mining

Strip mining of surface sulphur ore may be performed economically if:

(a) A sufficient orchody near the surface is defined, the thicker the better

(b) Overburden is minimal or absent

(c) Volume production is maintained.

Strip mining of coal at a rate of 400,000 tons per year can be very reasonable, not more than \$2.00 per ton. Lower costs for larger volumes.

Strip mining can be done on a long-term contract basis without owner's investment, provided long-term markets are available.

Since a section, one foot deep, of 60% sulphur contains 1,000,000 long tons of sulphur, worth \$40,000,000, a deeper deposit can be quite attractive economically.

#### POSSIBLY FRASCH MINING

The cover of the Lower Cretaceous consists of Loon River Shales which form quite an impervious caprock perhaps suitable for Frasch mining (melting sulphur with hot water) of an underground deposit of sulphur if one is present. Deeper drilling should be done to determine this possibility as well as surface sulphur.

Frasch mining requires no process pla nt except perhaps a molten sulphur filter.

Edward Lewis Jones and Associates

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#### ENGINEERING

#### 3. Processing

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D UTT JOITS

Several methods of recovery are available, but the one being used commercially in a California plant now, and that one experienced by the writer in Texas 15 years ago, consists of dissolving the sulphur in hot kerosene and filtering it from the gangue, and then cooling the solution so the sulphur precipitates.

This process has been written up in the attached article, along with others.

The cost of processing varies with the circumstances but is reliably reported to be not more than \$15.00/long ton of sulphur; comparable to average ... Frasch costs.

## A. Probable Costs

The cost of sulphur produced from a large deposit of 60% surface ore by strip mining and processing onsite is roughly estimated to be \$20/long ton. To this must be added transportation costs to railhead, which probably range about \$5.00 per long ton.

While sulphur sells for \$50/long ton and up, a cost of \$25/long ton is practical.

# Basement and surface sulphur abounds in Northern Alberta

### By Edward Lewis Jones Consulting engineer, Calgary

The discovery of surface sulphur in the Northwest Territories and Alberta may be the first step in the subsequent discovery of substantial subsurface deposits which may be amenable to Frasch mining, following developments in Texas.

#### Surface sulphur in Canada

A wide belt of quite pure surface sulphur from springs exists from Great Bear Lake and Great Slave Lake in the Northwest Territories to the Clearwater River in Alberta.

Largely these springs are on Devonian outcrops and they may well have been the origin of the surface sulphur deposits which have recently been discovered on the Peace River near Little Red River in Alberta.

The springs occur near faulted zones and it is also possible that the faults allow the circulation of waters to the surface, carrying up sulphur which may be broken out by permafrost, since sulphur is so friable.

Analysis of the surface sulphur in the Northwest Territories shows:

(1) No catalyst poisons such as arsenic, selenium and tellurium, which are very destructive to the life of the vanadium catalyst used in the sulpluric acid plants — the major use for sulphur.

(2) Up to 9S percent sulphur, with no metallic ions or hydrogen sulphide which might be associated with the sulphur in metallic sulphide deposits.

(3) The complete absence of sulphate reducing bacteria.

(4) A gangue material which is mostly calcium, carbonate, sand and silt.

The problem with the deposits around the surface springs in the Northwest Territories is that they are not extensive enough at any one location to support a mine, although some are within three miles of the railway.

The recent discovery of more extensive sulphur deposits on the surface near Little Bed River in Alberta, however, followed by an extensive land play amounting to more than three minion acres since October, suggests that much more be afoot. A comparison with the West Texas situation may be percinent. Comparison with West Texas

Fifteen years ago the writer was engaged on a plant project to process sulphur from surface ores (10 percent sulphur) from West Texas, in Pecos County (Oilweek, Nov. 20/67, page 72).

Today, the interest in West Texas sulphur is at its peak, and for the subsurface sulphur deposits.

Leases are drawing high prices. A 555-acre suphur lease in Culberson County in West Texas (the county adjacent to Pecos County) drew a high bid of \$1,056,323. A second 480-acre sulphur lease was bid at \$526,439.

Subserface sulphur is the great attrac on in this area (Wall Street Journ: 1, Oct. 29/67).

Apj. cently in Pecos County there is a 300-foot thick layer of elemental sulphur about S00 feet deep which is amenable to Frasch mining (Barons, August 1966).

The significance of surface sulphur deposits, in view of the thick deposit of elemental sulphur below the surface manifestations in West Texas, should not be overlooked in the exploration for sulphur in Alberta. Drilling to basement rock is the only sure way of determining the presence of sulphur, especially since the surface deposits appear to occur where there are faulted zones.

#### Recognition of sulphur

The surface deposits may easily be confused with elay, as well as with limonite, or yellow ochre. The burning of dry sulphur samples (ignition point,  $475^{\circ}$  F.) in air is well known, and is a sure test for sulphur with the characteristic royal blue flame and the pungent odor of sulphur dioxide.

However, sulphur may be red, brown and green, as well as yellow.

The deeper sulphur deposits at Ankerton, Alberta, have plastic sulphur which is dark green. A recognition problem exists.

Logs will show the presence of sulphur in well bores. A combination of three logs is required. This procedure was developed first, to the writer's knowledge, at Ankerton, and interested parties should contact Fred Halkow or E. E. Brownless, geologists and owners of the Ankerton deposit, for details on the detection of sulphur in downhole logs.

Requirements for mining sulphur

#### (1) SURFACE SULPHUR

Surface deposits of sulphur require sufficient sulphur for strip mining operations, both laterally and at depth, and preferably with a very low ratio of waste to ore, including overburden.

The thinner the overburden the better for low cost per ton of sulphur recovered.

The higher ratio of sulphur to gangue, the better. For strip mining coal, the figures are well worked out and well known. For a large-scale operation where ore mined costs \$2 per ton, the recovery of a 50 percent ore at that price would result in a sulphur cost of \$4 per ton. To this must be added the several costs of processing and transportation to market. Surface sulphur usually requires an extraction plant, which is not cheap.

#### (2) SUBSURFACE SULPHUR

The Frasch method of melting the sulphur downhole (as on the salt domes of the Gulf of Mexico area) requires fuel for hot water at 330° F., plus compressed air to lift the recovered pure brimestone in molten form.

The fuel requirements are not small. No less than 10,000 gallons of water per long ton of sulphur is sometimes required, although the better mines may require only 4,000 gallons per long ton.

Well costs are high, since stine domes require wells as close as 100 feet. Also bleed wells are required down-dip to remove cold water and improve circulation of heat to melt the sulphur. The reservoir heat balance must be right.

Lost water circulation down faults can also be a problem, which may be solved by mudding.

#### Conclusion.

The sulphur play in Alberta has tremendous possibilities for both surface and for subsurface deposits which may be showing on the surface. Owners of exploration permits for sulphur should consider deeper drilling to basement as well as exploring the surface deposits.

surrace depo

# TECHNOLOGY

sulphur

# 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 utlined below, rather than the

ers 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 marketa 'e sulphur. Volcanic sulphur, like that from sour natural gas, may be deposited by burning hydrogen sulphide.

Gco-bacterial reducation of sulphate Several kinds of bacteria can reduce sulphate to sulphur. Much comparison of isotope ratios in sulphur

> EDWARD LEWIS JOHES PRE-ESSIONAL ENGINEER

REGISTERED ALBERTA PRIMIES COLUMBIA OFFICE AMIA TELAD COLLEN COLLEN COLLEN COLLEN MORTANA N.B.E.R. CERT. #1928 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.

#### **Gcochemical** 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. G. Valensi (Contribution au diagramme potential-pII du soufre, Comp. rendu, 2cme 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 pII, 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:

$$KH_{3}S = (H^{+})(HS^{-}) \text{ or}$$
  
 $H_{2}S$   
 $(HS^{+}) = KH_{2}S = 10^{-1}$   
 $(H_{2}S) = (H^{+}) = (H^{+})$ 

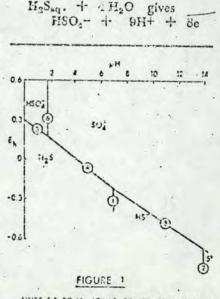
The equilibrium between the species . is one when pH = 7. Similarly,

$$\frac{(S--)}{(HS-)} = \frac{(H+)(S--)}{(HS-)} \quad \text{or}$$

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

and (S--) = (HS-) when pH = 24, so the boundaries between the specs s are vertical lines on the diagrar. at pH7 (Line 1) and pH14 (Line 2) regardless of electrochemical voltage.

However, oxidation of sulphurcontaining ions will be as follows:



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



$\begin{array}{c} H_2S_{aq}, +\\ SO_4 =\end{array}$	$4 \text{ H}_2\text{O}$ gives + 1011+ - Se
HS- + SO <sub>4</sub> =	4 II <sub>2</sub> O gives + 9II+ - 8e
S= <sub>aq</sub> . +	$4 \text{ Ii}_2 \text{O}$ gives $4 \text{ Ii}_2 \text{O}$ gives $4 \text{ SH}^+ + \text{ Se}$ .

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

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

Similarly, Line 4 for the boundary between  $SO_4 = \& H_2S$  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<sub>4</sub>-) and (H+) + (SO<sub>4</sub>=)

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

is line six at a pll 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  $\frac{(S=)(H^+)^2}{(H_2S)} = K = 10^{-21}$ 

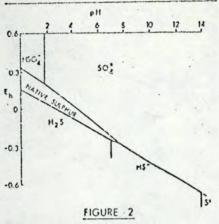
or  $\log S = = -22 + 2pH$ .

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<sup>-1</sup>, from the equations

 $H_2S_{aq} = \text{solid } S + 2H_{aq} + 2c$   $HS_{aq} = \text{solid } S + H_{aq} + 2c$  $S_{aq} = \text{solid } S + H_{aq} + 2c$ 

Solid S + 
$$4H_2O =$$
  
HSO<sub>2</sub>- $_{00}$  +  $7H_{-80}$  +  $6e$ 

Solid S +  $4H_2O =$ SO<sub>4</sub>=<sub>aq</sub> +  $8H_{aq}$  + 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 min.mal voltage differences.

Oth sulphides such as yrite can form alphur from water solution. Simile 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<sub>h</sub>---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 pII 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.

OILWEEK March 11/68

# TECHNOLOGY

production

# Sulphur recovery from surface ores

Discovery of apparently large reserves of native sulphur ore body in northern Alberta could result in the first substantial Canadian sulphur production other than from sour natural gas. Four Alberta sulphur prospecting permits covering nearly 80,000 acres have been issued in the Fort Vermilion area, and an undisclosed major company has entered into an agreement with Madison Oils and a private Calgary syndicate to explore and develop three of these permits. The following paper outlines some of the aspects involved in recovering sulphur from ore bodies.

## By Edward Lewis Jones, P.Eng. Consulting engineer

Fifteen years ago the writer engineered and constructed a small plant to recover sulphur of 99.5 percent purity from low-grade (10 percent) ores in Pecos County, West Texas.

The use of solvents to recover sulphur is well known. Sulphur will dissolve in a variety of solvents, usually best at its melting point of 246° F., such as: carbon disulphide, benezene, carbon tetrachloride, and aromatic petroleum solvents.

The process employs a number of steps which are common to all methods, no matter which solvent is used:

(1) St 'p mining of the sulphur ore.

(2) Crushing, grinding and screening to -20 mesh.

(3) Mixing with the lean solvent which is hot enough to heat the mixture to 250° F. (above the melting point of sulphur).

(4) Gangue separation to remove the solids from the sulphur-rich solvent.

(5) Solvent recovery from the gangue. The efficiency of this step frequently determines the economics of the process. The lower grades of ore increase solvent losses. Thus there is a lower sulphur limit, in any set of circumstances, which is the limit of economics corresponding to a given price for sulphur. Steaming is sometimes used to recover solvent from the gangue.

(6) Solvent distillation and sulphur recovery. Molten sulphur may be recovered by distillation of the solvent from it. The condensed solvent is re-used, after heating, to pick up more sulphur from the ore. Points to watch in such a process include:

(a) Solvent losses (to avoid drain of dollars).

(b) Suitable solvent selection to avoid the hazards of flammability and toxicity. Both are present with carbon disulphide. Carbon tetrachloride is highly toxic but not flammable. Both are expensive. A suitable aromatic petroleum fraction can be handled well without expensive losses and without serious contamination of the molten sulphur with hydrocarbons, yet with a reduced toxicity and flammability.

(c) Circulation rates. The science of extraction solids is well known, as are its disadvantages listed above. The range of sulphur solubility is from 10 percent to 15 percent in suitable petroleum fractions, depending upon the U.S. Bureau of Mines correlation index. About 0.5 percent to 2.0 percent residual sulphur remains in the recovered solvent for re-circulation in the process.

The solubility of the sulphur in the solvent crucially affects the circulation rate. It is evident that the circulation rates vary inversely with the solubility.

(d) Moisture. Any moisture in the ore requires a water draw tray in the distillation column, and a preliminary drying step may be necessary if the moisture percentage is too high.

#### Other processes

#### VAPORIZING

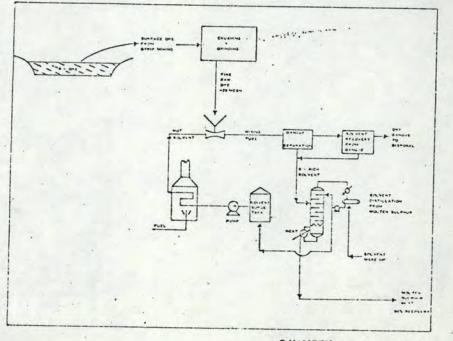
Sicilian surface deposits have been refined by heating, vaporizing the sulphur and condensing it to a solid. Usually part of the sulphur is burnt to provide heat, a very wasteful process.

#### FLOTATION

Certain flotation agents have been developed to recover sulphur from the surface ores. Then the process of autoclaving the flotation product to produce an acceptable product of suitable purity.

#### DIRECT OXIDATION

Surface ores in Nevada are burned with air to give sulphur dioxide in (Continued on page 74)



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# BOW VALLEY INDUSTRIES LTD.



Mr. Daryl K. Seaman, President, Bow Vailey Industries Ltd. announces the appoint-ment of Mr. Gordon B. Darling as General Manager of Alcon Petroleums Ltd., a wholly owned subsidiary of Bow Valley Industries Ltd.

Mr. Darling is a Petroleum-Geologist and a graduate of the University of Alberta. He has a background of 21 years of major company technical and management experience in the Canadian oil industry.

TEXAS GULF SULPHUR **APPOINTMENT** -athing

#### James W. Estep

Jomes W. Estop of Calgary was recently elected a vice-president of Texas Gulf Sulphur Company.

Market dan Songhan Company Mr. Ertop has being general man-ager of the Gos Division since it market its herdebarters from Vor-ond, Wwming to Calgary in 1963. In 2016 Physical le for the construc-d mar the two Tells solublar receivery d mar the two Tells solublar receivery places at Objects and Whitehautt,

#### SULPHUR RECOVERY

(Continued from page 72) a special burner which is then converted to supplierie acid for use in mining operations.

It is of interest to note this possibility for increasing the loading on the under-loaded  $H_2S$  conversion plants in the sour gas industry in western Canada:

 $2H_2S \div SO_2 \rightarrow 3S \div 2H_2O$ 

Problems of proper heat balance and avoidance of dust carry-over must be solved.

#### FERTILIZER

Recovery of sulphur dioxide from burning of surface ores may be done in ammonia solution. This can be performed to provide ammonium sulphate by well proven processes. Sulplate is 21-0-0, a welf known fertilizer acceptable in international trade.

The greatest demand is for sulphur - elemental brimstone --- for acid plants and for pulp and paper plants. Surface ores may be refined by solvents to yield acceptable brimstone in molten form. Each situation requires a detailed engineering study before the economics can be defined.



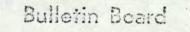
When I'm wearing strapless things Instead of buttons and bows, I notice that my boy friends Are always on their toes.

# 000

"If a lady preacher got married could you say that one man's mate is another man's parson?"

#### 000

Marriage is a process for finding out what sort of guy your wife preferred.



#### MEETINGS

Nev. 20 — Requesting Institute of Canada, Calgary Branch to how D. C. Floraing, director of Southern America Profilate of Technology, Carolina Restaurant, Calgary, 12 neon. Nev. 20 — Alteria Atsistentian of Petroleum Landance and Day matching, Pairloy Boys, Cal-awy, 3:50 p.m.

(a) State and State and State and State Society to hear D. M. al. high-and an endow of events to the following California Society of Petrological Comparison of the State and State and

Nov. 22 -- Conjury Research, CIMM to have the B. Saith distance potential nor condition particle Pation in understal and monetal resonance de-velopment in NE with and spend opportunities, Patherr Hintel, Colleary, 5:50 parts. Nov. 24 --- Instancement Institute of Catalog Calcus Branch to hear report on UNNs by J. F. Landston, J. Harma, F. G. Price, Al San Chilo, Calcury, S. prin. Nov. 29 --- Studies conservation Mathematics

Nov. 29 -- Sulphar symposium, Highlander Hetel, Calgary, 9 a.m.

#### LAND SALES

Nov. 21 -- DMR sale of 22 permits, Adorta. Nov. 23 --- Indian Affairs Branch sam of per-adis and leases on force Alberta reserves, Cal-Pary.

Nov. 28 -- DMR sale of 12 drilling eservetiens, Edunauton.

Nov. 25 -- CMR sale of 48 Block & leaver,

Det. 12 --- Cald Sele of 45 Duck & Leave, Calgary, Dec. 12 --- Saskatchevela Department of Mar-tral Resources sale of 11 permits, 10 defining reservations and 40 leaves, Regime. Dec. 12 -- DMR sale of 14 P & NG reserva-

Dec. 13 -- CMR sale of 44 Block A iteases,

Calgary. Dec. 10 --- EMB rale of 13 leases, Edmonton.

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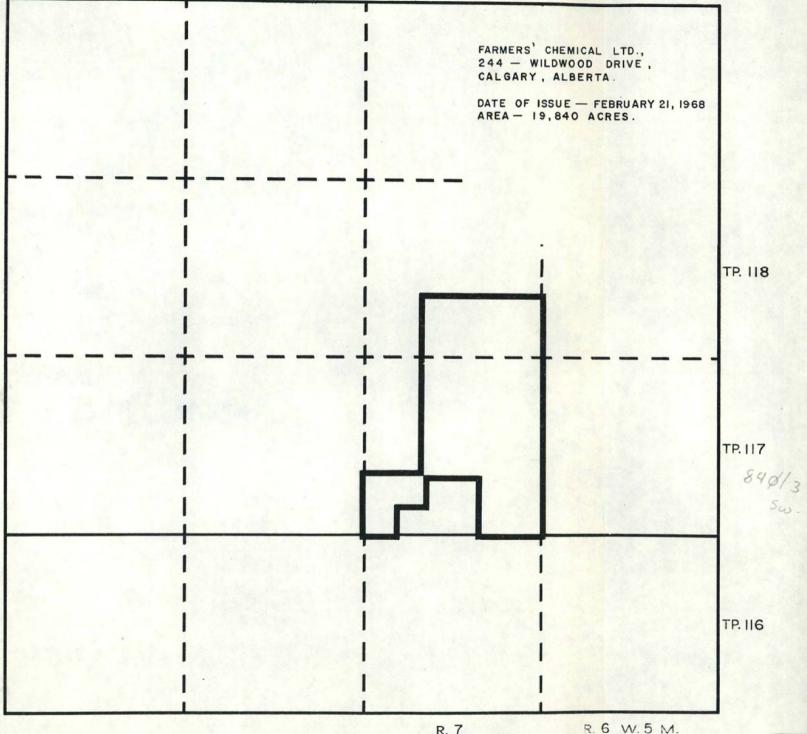
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# SULPHUR PROSPECTING PERMIT No. 173



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