Recent developments in sulphur mining by underground melting

Thermofluid mining of sulphur deposits

Bohdan Zakiewicz, Petro Z Corporation, El Segundo, California

The golden age of classical Frasch sulphur mining is fading away. In 1978, in an article in the 25th Anniversary issue of *Sulphur* the following view was expressed:

". . . during the next 10 or 12 years, the ten Frasch mines now operating in Texas and Louisiana will all get older, and each, as the years go by, will be consuming more and more gas for every ton of sulphur it produces. Sharp increases in gas prices are likely during this period, and many of those mines will have to close as they become uncompetitive with imported recovered sulphur and cheap, hydrodynamically-mined sulphur from the vast deposits in Poland – so many, we believe, as to make it unlikely that US Frasch sulphur production in 1990 will even approach the 5 million tons postulated in one recent forecast.

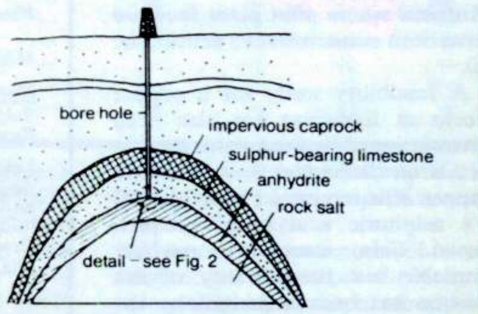
The Frasch sulphur mining industry of the United States is, indeed, fast approaching a parting of the ways; the choice between death and rejuvenation is not a difficult one to make. Let us hope that it will be made in time to save some of the needlessly large quantities of badly needed natural gas and sulphur which will otherwise be wasted."[1]

And, as forecast, the deterioration of the Frasch industry continues, resulting in the closure of Frasch sulphur mines. The reality of today's world economics does not leave room for sulphur mining operations based on the classical Frasch process, and even high sulphur prices can hardly revitalize the old Frasch mines that were closed due to high energy consumption. Further, new salt dome deposits, which, particularly in the initial stage of sulphur extraction, were ideally suited for exploitation by the Frasch process, and which, given suitable economic circumstances, could still be exploited using the process, are no longer known in the world.

Frasch sulphur mining

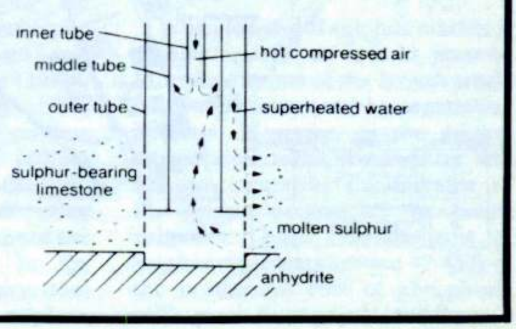
To understand the situation more clearly, a brief examination of the classical Frasch method is warranted. The process was developed to recover sulphur found underground in the vicinity of the Gulf of Mexico, where particular geological formations exist and sealed cap rock occurs. The geological structure underlying the area is a deep sedimentary basin, with Cretaceous strata underlying deposits of sand and clay. In places intrusions of rock salt from lower levels have distorted the Cretaceous layers forming "salt domes" (Fig.1). Overlying the salt are layers of anhydrite, dolomite and limestone, the so-called "cap rock". The anhydrite and Tertiary clays over the limestone are effectively impervious and sulphur is found dispersed through the dolomitic and limestone layers.

Fig.1: Structure of a Sulphur Dome



Where the sulphur can be economically exploited, a well is drilled through the cap layers and the sulphur-bearing layers down to the top of the anhydrite stratum. Three coaxial pipes are then introduced into the bore hole (Fig.2). The outermost pipe, which reaches to the bottom of the borehole, is perforated with slots at its lower end. The middle pipe is somewhat shorter, ending about half way down the perforated part of the outer pipe. A collar on the end of the middle pipe closes off the annular space between the two pipes from the space below the end of the middle pipe. Water at about 165°C under sufficient pressure to keep it from boiling is forced down the annular space between the outer and middle tubes, through the perforations in the outer tube above the collar and into the deposit. The water melts the

Fig.2: Operation of the Frasch Sulphur Recovery System



sulphur around the pipe end and pushes it through the bottom openings of the outer pipe into the middle pipe. As sulphur has about 1.8 times the density of water, it collects at the bottom of the borehole and will only rise about half way up the middle tube under the influence of hydrostatic pressure. Hot compressed air is injected through the innermost pipe, which extends about two thirds of the way down the borehole and therefore ends well below the surface of the sulphur column in the middle tube. The resulting foam of sulphur and air is very light and rises easily the rest of the way to the surface. At the surface, the sulphur froth is deaerated and the sulphur separated.

In the real world, things are often less than perfect, and many underground native sulphur deposits do not occur with sealed cap rocks. The geology may be faulted or, for other reasons, the mine process water and melted sulphur may be able to escape the formation without being raised to the surface. Such deposits can only be exploited if the classical technology is adapted in some way to compensate for these drawbacks.

It is the case that most of the underground native sulphur mines which exist outside of the Gulf of Mexico (for example, Poland, the USSR and Iraq) have had to utilize an underground mining technique that is an adaptation of the classical Frasch process, in order to limit water and heat consumptions to acceptable levels. Similarly, adapted technology may be useful in rehabilitating old workings that have been closed because water and heat consumptions had become excessive.

Working old deposits

As outlined, with the high costs associated with the Frasch technique because of the high energy requirements, many mines have closed. However, significant amounts of sulphur are still left in the abandoned mines, and it is estimated that in the United States there is still more than 100 million tons of sulphur in those deposits mined using the classical Frasch method. An obvious question is, therefore, can the sulphur that remains be recovered economically?

To answer this has necessitated studying the hydrogeological and economic aspects of the American sulphur deposits. It has also been necessary to take into account the hydrodynamic technique for mining native sulphur deposits, a technique proved in 1966 on an industrial scale in Grzybow, Poland. The commercial adaptation of this technique resulted in the subsequent development of the Polish and Iraqi sulphur mining industries.

This year is the 20th anniversary of the use of the hydrodynamic process for continuous, economic production of sulphur from six so-called "non-fraschable" deposits. A feature of these deposits is that energy consumption is only one-third of that in the twenty Frasch mines abandoned in the United States. The total amount of sulphur recovered using the hydrodynamic process over the past twenty years is approaching 100 million tons. The sulphur recoverability factor was not less than 75%. A comparison of the quantities of sulphur recovered by the Frasch and hydrodynamic techniques is shown in the Table.

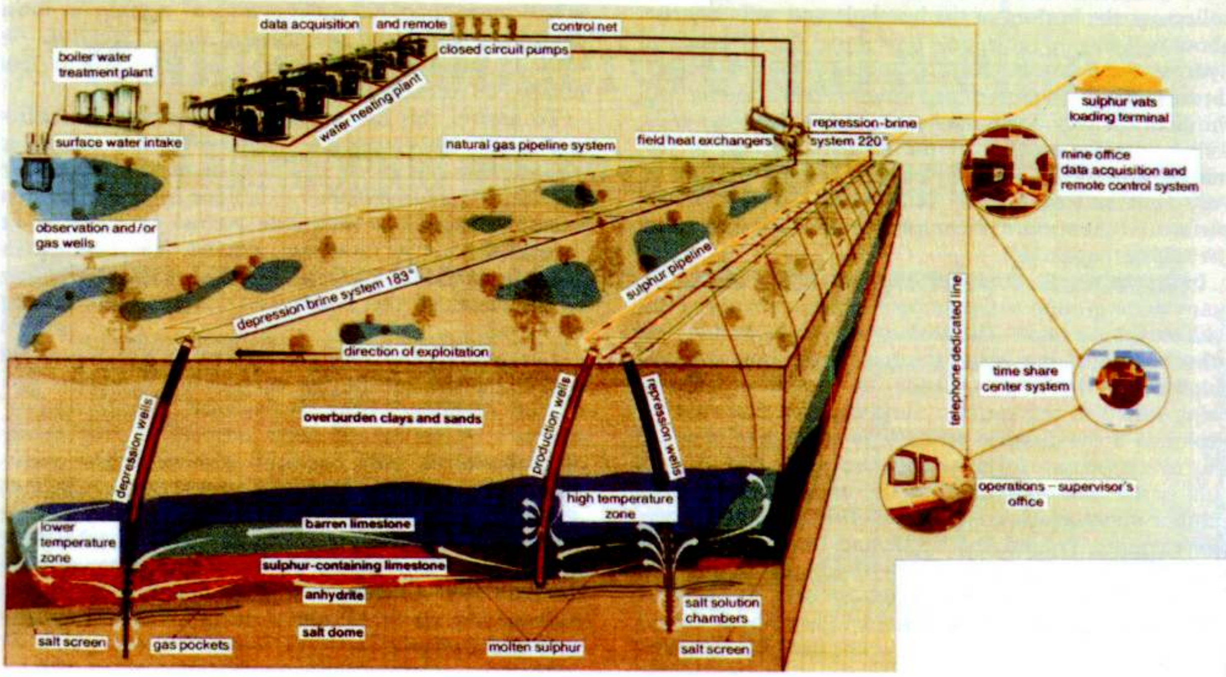
The study of the American sulphur deposits and the addition of new inventions, enhancements, and improvements to the original hydrodynamic process has resulted in the development of thermofluid technology – a novel process specifically intended to enable economic redevelopment of the partially-depleted sulphur salt dome deposits and the exploitation of difficult non-

Underground Bore-Hole Mining of Sulphur

Company	Mine	Date on stream	1985 annual production ('000 tons)	Process used*
USA				
Texasgulf/SNEA	Boling Dome	19 Mar 1929	400	F
Pennzoil Sulphur/Duval	Rustler Springs	30 Sep 1969	2,200	F/HD
Freeport McMoRan	Garden Island Bay	19 Nov 1953	F	
Freeport McMoRan	Grand Isle	17 Apr 1960	2,400	F
			Total 5,000	
Iraq				
National Iraqi Minerals Co.	Mishraq	1972	700	HD
Poland				
Polish government	Grzybow	June 1966	900	HD
	Jeziorko I	1967	500	HD
	Jeziorko II	1967	3,000	HD
	Basznia	1975	20	HD
			Total 4,420	
Mexico				
Azufrera Panamericana	Jaltipan	n/a	520	F/HD
CEDI	Texistepec	n/a	600	F/HD
APSA	Coachapa	May 1981	260	? F
APSA	Petapa	30 Sep 1984	120	? F
APSA	Otapan	1986	—	? F
			Total 1,500	
USSR				
Soviet government	Jazovsk & Others	1969	1,500	HD
	Total World bore-hole production		**13,120**	
	Frasch process production (37%)		***4,840***	
	Hydrodynamic process production (63%)		***8,280***	

* F – Frasch process; HD – Hydrodynamic process

Fig.3: Hydrodynamic Exploitation of a Partially Depleted Sulphur Dome



conventional bedded-type deposits world-wide. Highlights of this technology are:

Low cost of energy input and low operating cost.

High sulphur recoverability ratio from old or new deposits.

Low capital expenditure due to the application of light modulized, mobile mining equipment.

Insignificant or manageable environmental impact.

Basic features of thermofluid mining technology

The proprietary thermofluid technology for sulphur mining incorporates all the elements of the hydrodynamic process used in large scale mining operations (Fig.3). In addition, it incorporates modifications and techniques that make it particularly suitable for use in depleted salt dome deposits. The basic process components are shown below.

Multi-well system

The basic construction of the multi-functional production wells for sulphur extraction and the multi-well system, consisting of the long parallel rows of wells to form a narrow belt at the exploitation front, are the same as in the hydrodynamic configuration. Depression wells, which are aligned parallel and close to the exploitation front are extended in their depth to reach the salt formation and dissolution of the salt, known but rarely applied in the past, is a key component of the thermofluid process (Fig.4). In the initial phase of preheating of the deposit, additional rows of water and flue gas injection wells may be drilled to reach the salt formation. This accelerates the dissolution of the salt and stimulates the flow of brine in the deposit.

Well stimulation system

A new well stimulation system, based on oil well practice, has been introduced. High-velocity explosion is replaced by propellant deflagration, which is used to rubblize the solidified sulphur in the lower part of the formation. The fracturing-rubblization process can be repeated at anytime in each well without extracting the production tubulars from the inside of the well, because there is no need to place the propellant charge down the well. The wellhead is constructed so that it is possible to attach a cannon barrel, which, at the surface, serves as a propellant combustion chamber.

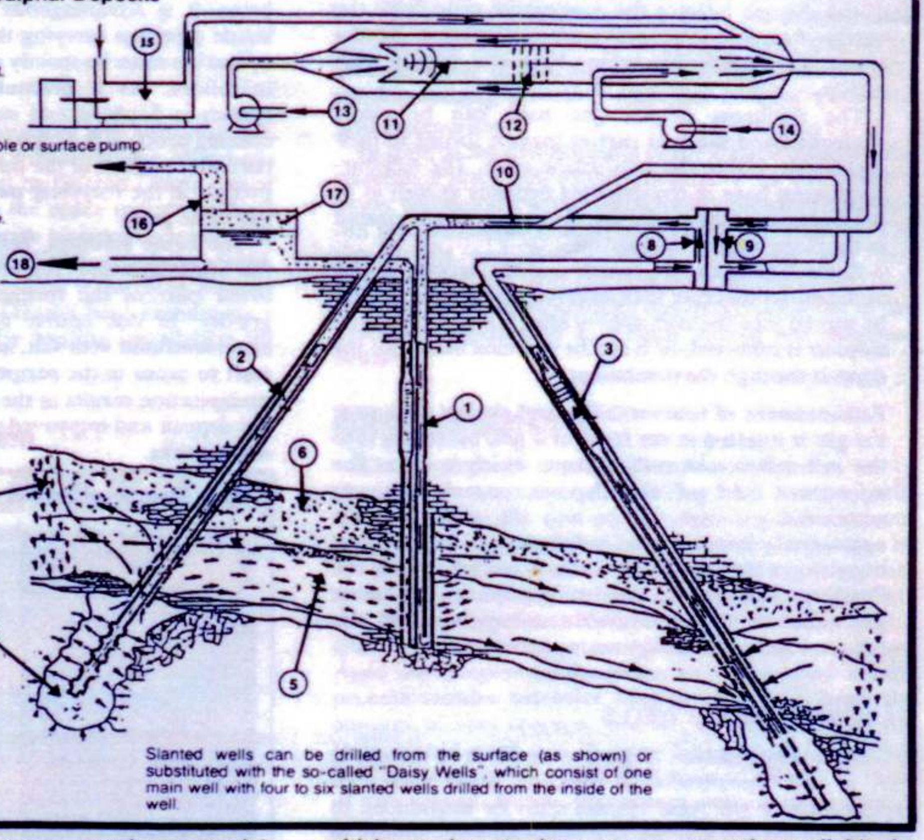
Well pumping system

The mining media is brought to the surface using two pumping systems. A conventional air-lift pumping system is used to pump sulphur from the production wells. The second pumping system is employed in water-brine extraction.

In the thermofluid process the relatively cold compressed air commonly used in other processes is replaced by hot flue gases. This allows wells of low productivity, which previously were killed by solidification of sulphur when large amounts of colder air were injected, to be operated. The gas lifting is performed either through a dedicated internal tube or by means of a controlled partial liberation of the compressed gas from the gas cap into the gas lifting tube. The gas cap is developed in the upper part of the deposit by injecting both flue gas and preheated water from the combustor-heater.

Fig.4: Thermofluid Mining of Sulphur Deposits

1. Sulphur production well with gas-lift.
2. Water/gas injection well.
3. Brine extraction well with submersible or surface pump.
4. Salt solution chamber.
5. Sulphur melting and brine flow zone.
6. Gas cap.
7. Salt precipitation zone.
8. Heat exchanger for brine recycling.
9. Flue gas heat exchanger.
10. Flue gas quencher/mixer.
11. Thermofluid combustor/heater.
12. Catalytic reactor.
13. Fuel pump.
14. Water injection pump.
15. Fresh air compressor.
16. Gas-lifting flue gas scrubber.
17. Sulphur – gas separator.
18. Molten sulphur outlet to storage.



Slanted wells can be drilled from the surface (as shown) or substituted with the so-called "Daisy Wells", which consist of one main well with four to six slanted wells drilled from the inside of the well.

The water-brine extraction system requires a special type of submersible pump, which has been developed in co-operation with one of the leading US manufacturers. It is resistant to a temperature of 180°C, and can maintain the pressure necessary to recycle the brine through the heat exchanger and introduce it into the production system and special injection wells. In shallower mines, the submersible pumps can be replaced by surface pumps, with the same results being obtained through a one-stage brine recycling pumping system.

The heat energy system

The key element in the thermofluid heat energy system is the closed-loop recycling of the heat carrier within a narrow belt at the exploitation front. This results in a high concentration of heat per unit volume of the deposit and a high velocity flow of the heating media.

The combustor-heater

The proprietary high-pressure combustor used in the process was developed following six years of research and testing. The main features of the combustion technique used are the control of fuel atomization and catalytical combustion of low-value hydrocarbon fuel by emulsifying it with a large excess of water. The combustor can be fuelled with a mixture of gas and liquid fuel, low heat value syngas, methanol and, most importantly, it can use waste crude, resids, tars, rejected oil, cleaning solvents, toxic combustibles, etc., all of which are inexpensive sources currently available in abundant amounts and which in addition create significant environmental pollution problems.

The combustion system, utilizing the low-cost fuel material, has accomplished the following:

complete, clean, catalytic combustion of the low-cost energy source;

direct pollution-free injection of hot combustion products into the deposit.

It is also a highly reliable modular design that is mobile, compact and low-cost. The combustion system is computer controlled, as are the wells and the entire mine operation.

Recycling and reheating system

Closed-loop recycling of the heat carrier results in major heat economy, not only in this case but in any heat consuming mine operation. The basic engineering and know-how used in the thermofluid process is the same as that in the hydrodynamic recovery process. In addition, the thermofluid process features simultaneous injection of flue gas together with superheated brine.

FLUE GAS RECYCLING SYSTEM

The injection of the flue gas results in the following:

Increased heat efficiency: an additional 17-25% of the heat is employed in the deposit instead of being vented into the atmosphere.

Reduced heat losses: the gas created in the upper part of the deposit isolates the productive zone from the barren formation by preventing saturation of the barren formation by brine, here the major heat carrier.

The thickness of the gas zone can be easily controlled and the heat carrier may be forced to flow exclusively within the production zone. The sulphur-containing zone in the depleted deposits as well as in the majority of the virgin salt dome deposits is located in the lower part of the deposit.

Some 10% of the gas forced into the deposit will be pumped out together with sulphur, this gas may either be vented into the atmosphere after it is scrubbed and sulphur is removed, or it can be recycled back into the deposit through the combustor.

Enhancement of recoverability and energy economy: the gas is injected in the form of a gas/brine mix into the salt solution chamber, from which it ejects the uppermost part of the deposit, namely the gas saturation gas cap. On its way the gas/brine mix aggressively invades the sulphur-containing zone, triggering a turbulent flow of fluids and improving the "washout" process for displacing sulphur. The above gas action is highly desirable, enhancing both the recoverability and energy saving processes.

GAS CAP BLEEDING WELLS

Since a large amount of gas accumulates in the upper part of the deposit after a relatively short period of exploitation, a gas relief system must be introduced to control the gas cap volume. Gas bleeding wells, similar to the Frasch water bleeding wells, are installed. These wells are positioned at the periphery of the deposit and equipped with localized or centralized scrubbing equipment. The flue gas composition is approximately 20% carbon dioxide and 80% nitrogen, plus minor amounts of impurities. The bulk of the impurities, the composition of which depends on the source of the fuel, undergo a self-cleaning process as they filter through the hot, carbonaceous deposit.

WATER-BRINE RECYCLING SYSTEM

The decompression wells that extract the water-brine solution are operated by a submersible or surface pump, which constitutes the heart of the system. The recycling system is completely self-contained on the surface. The advantages of brine recycling are:

the brine is pumped out at a controlled 80-90°C, which represents over 50% of the heat energy required for sulphur mining;

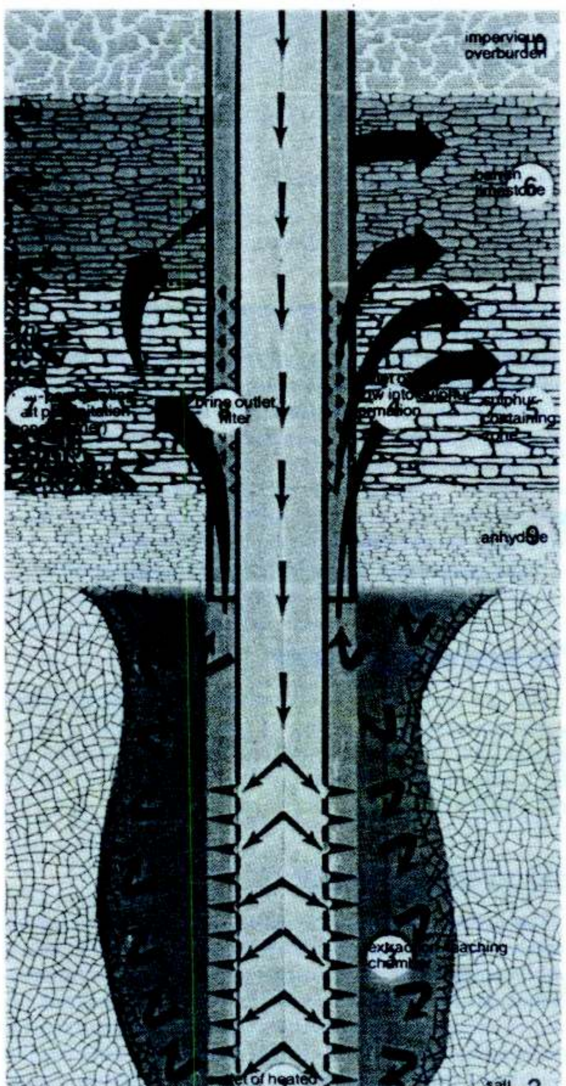
recycling through the salt solution chambers leads to salt saturation, which in turn eliminates carbonate hardness and scaling;

in most cases saturation with 20% sodium chloride increases the scaling point temperature of the mine water, which is highly susceptible to scaling, from 54°C to 160°C. The same level of saturation of the mix with sodium chloride and potassium chloride may shift the scaling point up to 180°C, which is adequate for any sulphur mine reheating system.

In the initial period of recycling the semi-saturated brine, it is advantageous to create a coating of scale inside pipelines carrying the heating media. This type of operation must be strictly monitored and supported with inhibitors. As a precautionary measure, the piping system is doubled and designed in parallel. The scale coating protects the pipe system from hydrogen sulphide corrosion, which in the initial stage of separation will be present in the recycling media, and later replaced by the inert flue gases.

The brine solution, being substantially heavier than the brackish water, replaces the deposit water from the lower part of the formation by the natural force of gravity. In due course all of the hot brine becomes supersaturated with salt, and precipitation of the salt will start to occur in the peripheral parts of the deposit. This precipitation results in the formation of a solid barrier in the deposit and improved containment of heat within the mining area.

Fig.5: Diagram of the Salt Chamber for Brine Preparation



A large water installation, required by the Frasch process, is not required.

HEAT EXCHANGE SYSTEM

The thermofluid process replaces the conventional, bulky tubular heat exchangers with very light, liquid-gas heat exchangers, manufactured by Garrett Corp., one of the largest manufacturers for the space industry. These heat exchangers are charged with high-temperature flue gases (the heat carrier) and with the brine to be reheated. The combination of the two systems – the clean no-soot flue gas combustors and the Garrett heat exchangers – gives an outstanding, small-size heating installation for large production capacities.

The Gasobarriering system

As previously mentioned, the flue gas cap in the deposit is created to prevent loss of heat to the overlying barren and overburden formations. In the case of salt dome sulphur deposits, such a gas cap efficiently substitutes any need for additional heat containment, and together with the spontaneous precipitation of salt and self-formation of a solid salt barrier, the heat containment in the majority of small deposits is ideal.

In large, abandoned salt dome deposits, as well as for bedded deposits, a special mining technique called the Gasobarriering system can be used. This system consists of a row of gas injection bore-holes and a compressor. A mixture of cooler post-scrubbing gas and air can then be injected into the deposit at a pressure higher than the pressure of the other material injected during mining. This procedure cuts off any major flow of injected material into the protected area and prevents major heat losses. In most cases, the differential pressure between these other injected materials and the "barriering" gas is sufficient if it is between 1 and 3 atm.

Mobile mining equipment

Thermofluid technology, when adapted to partially-depleted deposits, utilizes a proprietary, modulized, mobile assembly of mining equipment. The largest item in the system is the compressor, which was the smallest installation in the old Frasch mine. The combustor-heater is a light, skid-mounted unit that can be readily transported to the mining site and located in close proximity to the production wells, thus eliminating long heat transport lines and subsequent heat losses at the surface. The entire surface installation for a 300,000 t/a sulphur mine is not expected to exceed 2,500 tons in weight. Capital cost for such an installation, compressors and a small electricity generation plant included, should not exceed about US$6 million.

Practical application of thermofluid technology

Some of the major problems encountered in the Frasch industry and the ways they can be remedied have previously been discussed.[1,2] Very little has changed in the classical Frasch industry, except continued closing of Frasch mines. Outputs from the large Grand Isle and Boling Dome mines have dramatically declined, suffering high energy production costs. Only one mine, Rustler Springs, has improved its energy efficiency, due to the incorporation of a feature used in the hydrodynamic sulphur mining process – recycling of mine water and heat reclamation.

In spite of the deterioration of the Frasch industry, the classical Frasch philosophy continues to overshadow newer technology, which introduces radical changes that can lead to renewed economic recovery of sulphur. The Grand Isle and Boling Dome mines are the "last Mohicans" of the large salt dome operations in the USA. How thermofluid technology can overcome some of the problems experienced in Frasch mining are discussed below.

Energy consumption

The concept of cogeneration has received a lot of attention as a means of offsetting high energy costs, mainly due to the favourable attitude of the current legislation. Whether this concept will have long life or be crippled by future State and local regulations, or by other factors, is uncertain. But cogeneration does not alleviate the high energy consumption per ton of sulphur and cannot be the answer to uneconomic mining operations. Aged mines operated according to the classical Frasch process require extensive heating. In some cases the amount of heat required per ton of sulphur recovered from an old mine is 5-20 times higher than that which had been necessary in the initial stage of mining. In most of the closed mines, the energy cost escalated from 15-20% of total production costs in the initial stage of exploitation up to 85-90% (for example, the Chacahoula, Fannett, and Long Point mines).

In the past, many attempts were made to decrease the permeability of the barren formation to prevent heat loss; mud injection ("Mudding") was carried out at Hoskins Mound, but was too costly to become effective. Thermofluid technology offers new techniques leading to decreased energy consumption which include:

recycling of the mining solution;

switching from natural gas to lower-cost fuel;

"barriering" to stop excessive water/heat losses.

Sulphur recoverability

There will be no secondary production of sulphur from old, abandoned deposits if the recoverability ratio stays at the classical Frasch level. The major reason for the relatively low level of recoverability is the loss of heat into the upper part of the barren formation and heat soaking instead of dynamic displacement of superheated water and sulphur from the deposit. What currently occurs is that, after being melted, a substantial volume of sulphur is re-deposited in the lower part of the deposit and impregnates pores which were initially open for filtration of water and liquefaction of sulphur.

Numerous laboratory and field tests in the production areas have proved that the Frasch process can ideally recover 70% of the original sulphur when mineralization is within the 5-10% range, and that 30-35% recovery can be expected when mineralization ranges from 15% to 28%. Mineralization in the USA deposits is predominantly within the latter range. The majority of old mines have reached 35% sulphur recovery, the physical limit of recoverability using the Frasch process, particularly in almost parallel sulphur zones. In the productive zone, located on the slope of the dome, improved recovery may occur if the boreholes were adequately condensed.

The thermofluid process offers techniques to improve sulphur recoverability, which can be accomplished through:

increasing the specific gravity of the melting media in relation to the water in the mineral deposit; this in turn results in gravitational separation of the preheated flowing media from the stagnant, cooler, deposit water.

increasing the penetration of the heat-carrying media into the lower part of the formation.

developing a dynamic flow of that media through the pores to force displacement of molten sulphur using kinetic energy provided by the turbulent action of the melting media.

developing constant dynamic or static barriers and containment of the heated media in the deposit.

Capital investment

In order to justify investment in Frasch mining operations, it is imperative to have large reserves of sulphur. Another criterion is a fairly high sulphur content in the deposit, not less than 5 tons/m^2. For a medium-size operation of 300,000 t/a of sulphur, the minimum mineable reserves should not be less than 2.1 million tons and the total original reserves not less than 6.0 million tons. In practice, it is very difficult to find such a deposit among known sulphur deposits in the USA.

Capital investment and start-up costs for the hypothetical mine (300,000 t/a) are estimated to be approximately US$30 million. Assuming a sale price of $130/ton of sulphur (ex-mine), mineral rights royalties not higher than 15%, production costs not exceeding $70/ton, taxes not higher than 35% with depletion allowances, and return on investment of 5 years, the ultimate interest earned by the investor on the capital invested would be about 18%/a, providing the investor operates the mine and does not share the profit with a contracted operator.

The above criteria are, however, rather optimistic. Production cost at the Long Point mine has approached $100/ton, which caused its closure.

For any partly-depleted deposit in the USA the investment in classical Frasch operations would be difficult to justify. As outlined, though, investment for an operation using thermofluid technology is much less.

Environmental impact

The adaptation of thermofluid technology significantly eliminates most pollution problems, despite the fact that highly polluted fuel is used as a basic source.

On the surface:

hydrogen sulphide contamination is eliminated because a closed-loop recycling system is used. No mine water is disposed of to ponds or other surface waters, as is the practice when the Frasch process is used;

water treatment wastes, post ion exchanging brine, are eliminated in the thermofluid process;

flue gas emissions into the atmosphere are eliminated;

subsidence of the surface due to secondary exploitation mines causes less damage because primary consolidation of the formation has already taken place (some subsidence will still occur);

pollution from pulverized sulphur is eliminated as sulphur is pelletized at the mine site.

Sub-surface:

underground migration of hot, toxic water is largely contained to the mining area and the recycling system;

pollution of ground water aquifers is contained to within the vicinity of the mining operations, although some pollution is likely to occur;

migration of molten sulphur with eruption to the surface is highly improbable due to the recycling and containment systems.

Potential use

If thermofluid mining were used, it is believed that five or six abandoned Frasch mines, each with a capacity of 250,000-350,000 t/a of sulphur, could be restarted and operated economically. The average capital cost of erecting the mine is estimated at $10-15 million, while the cost of energy (including the compressor and electric power) is expected to be below $10/ton of sulphur. It is also claimed that three mines could be built simultaneously with an average engineering and construction time of about ten months and equipment delivery within six months. □

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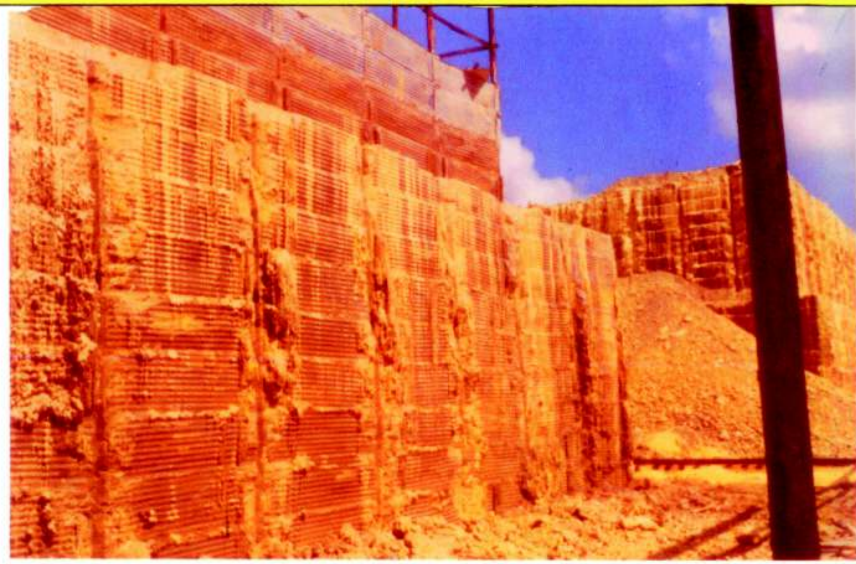
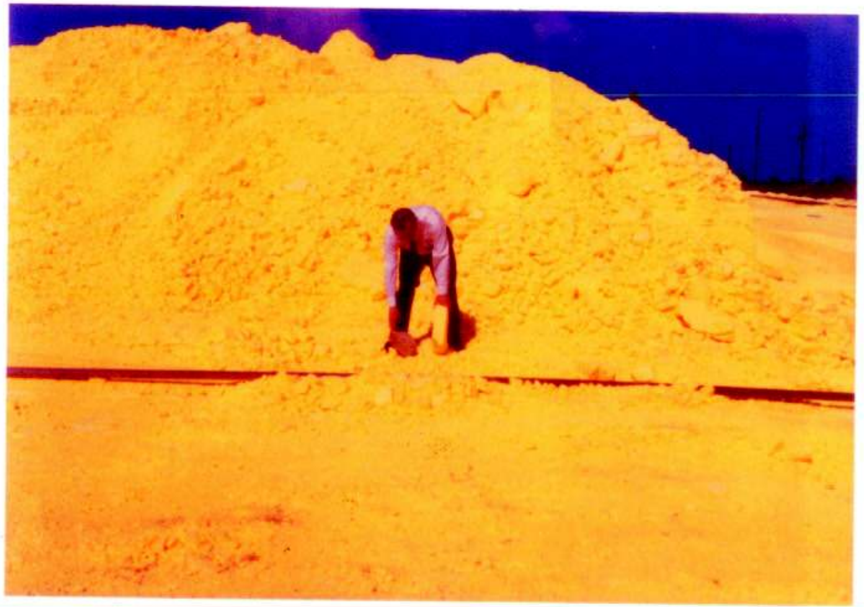
SIX SULPHUR MINES COMPLETED IN 5.5 years from the START In 1966, BASED ON PATENTED WORLDWIDE THE THERMO-HYDRO-DYNAMIC TECHNOLOGY, INITIATIVE AND LEADERSHIP OF BOHDAN M. ZAKIEWICZ. Total PRODUCTION: 6,200,000 T/Y. RETURN ON INVESTMENTS: 2 YEARS FOR EACH MINE

SULPHUR MINE JEZIORKO I , POLAND, 1,200,000 T/Y , 1968



TWO SULPHUR MINES-JEZIORKO II and III, POLAND, 2,500,000 T/Y. 1969

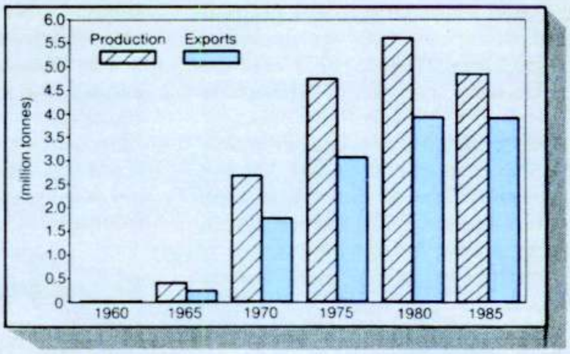
FIRST BZ SULPHUR MINE, GRZYBOW, POLAND, 1,000,000 T/Y, 1967



SULPHUR MINE-MISHRAQ, IRAQ, 1,200,000 T/Y, 1970

Poland

25 years as a sulphur exporter



Sulphur production in Poland has a long history dating as far back as the fifteenth century, but it is only since the late 1950s that Poland has begun to exploit on a large scale its vast sulphur reserves. The intervening years have seen Poland rise to become the world's third largest sulphur producer and second largest sulphur exporter. 1986 is Poland's 25th year as a sulphur exporter and to mark the occasion, this article reviews the development of the Polish sulphur industry and considers some of the factors contributing to its growth.

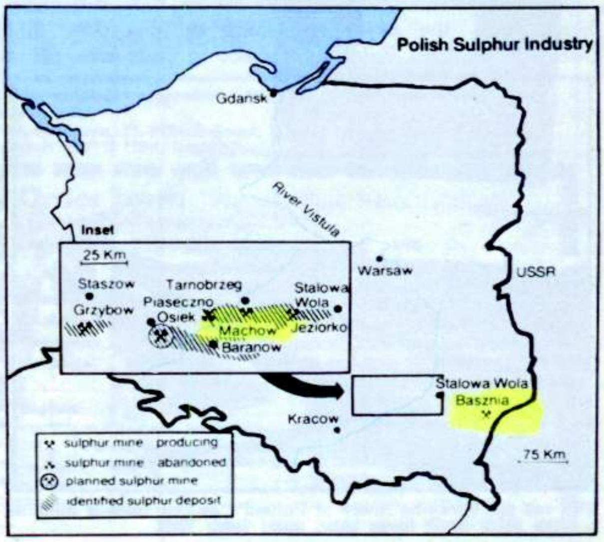
The first theories regarding the existence of rich deposits of sulphur bearing ores in Poland were made during the 1920s. Further studies followed, culminating in an exploratory programme led by Dr Pawlowski and funded by the Polish Geological Institute in Warsaw, which confirmed the existence of sizeable deposits in 1954. Reserves of over 500 million tonnes were identified in a belt 250 kms long, running from Krakow in the west to the Russian border in the east.

Poland's first sulphur mine at Piaseczno in the Tarnobrzeg region was inaugurated in 1957, and operated until 1971 when it was closed due to depletion. The mine was located in the Vistula river valley and an unconventional multiwell barrier system was developed by Dr B. Zakiewicz to enable open pit excavation of the ore body from under the highly permeable sand gravel formation of the Vistula river valley. Average production from the Piaseczno mine was around 285,000 t/a, and in 14 years total production amounted to 4 million tonnes.

The exploitation of sulphur reserves at Piaseczno enabled Poland to enter the sulphur export market. Polish exports of sulphur began in 1961 at 41,500 tonnes, and rose steadily to reach 271,900 tonnes in 1966 accounting for 57% of production. The main market for Polish sulphur during the early 1960s was Poland's neighbour, Czechoslovakia, which took around half of Poland's exports between 1961–1965. A steady increase in production from Piaseczno also enabled Poland to decrease imports which fell from 35,845 tonnes in 1960 to only 7,000 tonnes in 1965 before ceasing altogether.

The impact of new technology

The most important development in the domestic sulphur industry regarding Poland's emergence as a leading sulphur producer and exporter was the development of the "Thermo–Hydrodynamic" method of mining sulphur – a modification of the conventional Frasch process which enabled the exploitation of unconfined deposits in Poland which could not be mined using the traditional Frasch process. The new method was invented and pioneered by Dr Bohdan Zakiewicz, head of the Geopol engineering company. Despite its eventual success, the Thermo Hydrodynamic method did not, at first, meet with government approval, and initial tests on the Grzybow deposit by Geopol in 1958 were carried out without the knowledge of the Ministry of Chemical Industry. However, when the results of the tests came to light, the Minister of the Chemical Industry set up a research and development department in Krakow – "Hydrokop", to further develop the process. Tests continued for a further nine years, delayed by difficulties in obtaining funding, and culminated in the production of sulphur from the pilot Grzybow mine where reserves were estimated at 16 million tonnes on 1 June 1966. The Grzybow mine was fully developed during the next eighteen months, and another mine using the Thermo Hydrodynamic method at Jeziorko was inaugurated in 1967 with reserves estimated at 220 million tonnes of recoverable sulphur.



highest, although it has been identified in virtually every major country of the world. According to the Sulphur Institute, the number of Asian countries recognized as sulphur deficient doubled from 1960 to 1977 and the number of states in the USA reporting crop responses to sulphur fertilizers rose from 13 in 1962 to 35 by 1981.

In India and Indonesia in 1980 the amount of sulphur taken up by field crops was estimated to be 784,000 and 130,000 tonnes S respectively.[6] The application of S by fertilizers was put at 250,000 and 48,000 tonnes, which would indicate that large sulphur deficits are occurring, and overstraining soil reserves to the detriment of crop production.

The sulphur nutrient – an economic choice?

It can be seen that while the application of sulphur can ıave a significant impact on crop yields and is beneficial n both human and animal nutrition, it has been ıeglected in agricultural development programmes. This :an partly be attributed to a lack of information on its :conomic significance.

In the past the S-component of fertilizers was often ignored and treated as an "extra". However, an Indian study[7] has shown that when the sulphur content is ncluded, the calculation of fertilizer price by nutrient gives a 27% lower price of N for AS and a 25% lower price of P for SSP. This fact is now more widely recognized in the United States where there has been a rend towards the use of ammonium sulphate and granular elemental sulphur by blenders of compound fertilizers.

The major factor inhibiting full recognition of the sulphur deficiency problem, is the absence of comprehensive statistical data on its occurrance.

The Sulphur Institute has responded to this by announcing recently that it intends to concentrate all its resources on the issue of sulphur in agriculture. However, only when the farmer is persuaded to view the economic returns from applying sulphur as being within the same parameters as NPK application will sulphur be truely considered the fourth major nutrient. □

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Morocco and Tunisia reduced their requirement reflecting the depression in the world phosphate market. Deliveries to Eastern Europe rose 2% with Czechoslovakia and Yugoslavia increasing offtake, whilst deliveries to the USSR slipped slightly.

Around 60% of Poland's sulphur exports are made in the form of lumps; liquid sulphur exports comprise approximately 30% of the total, with the rest in granules or powder. Western Europe is the major customer for liquid sulphur exports, shipped via the Port of Gdansk. Hungary, East Germany and Czechoslovakia also receive liquid sulphur from Poland.

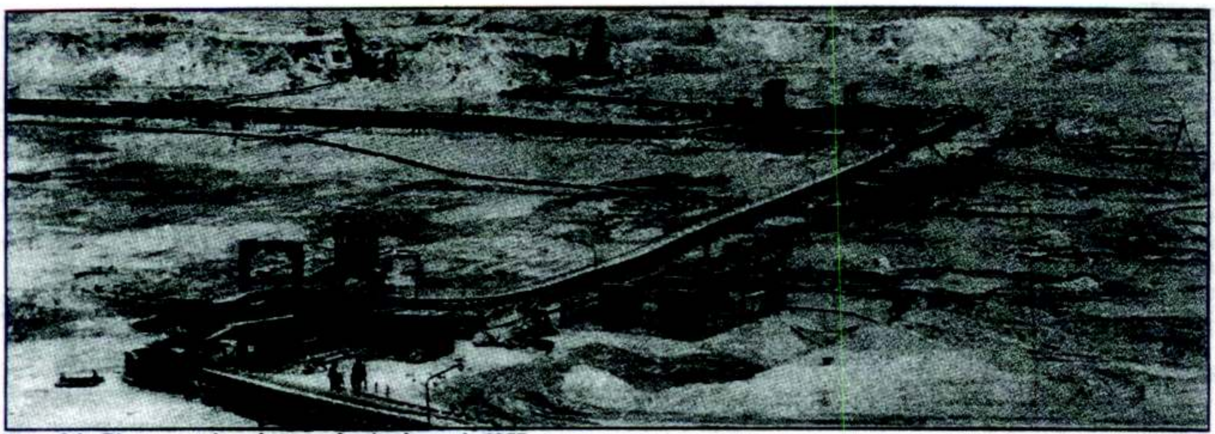
Lack of investment – a problem in the 1980s

The major factor behind the stagnation of the Polish sulphur industry, in particular since 1980, has been a lack of investment in new production capacity as a result of the crisis in the economy. The Grzybow mine is nearing the end of its productive life, but problems with obtaining finance for further development have continually set back plans to exploit other deposits. Towards the late 1970s it was recognized that construction of a new mine would be necessary to meet domestic demand and maintain exports, but it was not until 1985 that finance became available to construct a new mine at Osiek on the west bank of the Vistula river to exploit reserves in the Baranow area parallel to the Jeziorko deposit. Ciech Co. Ltd., which handles Poland's sulphur exports, will participate in financing the Osiek project, where initial production is expected to commence in 1988, reaching full capacity of 1.2 million t/a in 1990.

Delays in implementing the new mine at Osiek and the emphasis placed on maximizing production from existing sources to boost earnings on the back of rising sulphur prices have meant that planned production turndowns at Grzybow have also been delayed. It was originally envisaged that output from Grzybow would be reduced to just the 0.3 million t/a required by the carbon disulphide plant on site in order to prolong the life of the mine. However, the need to maintain export levels has meant that production at Grzybow has instead been maintained at around 0.8 million t/a.

Future prospects

While delay in investment in new mining capacity may restrict availability of sulphur on the export market until 1990 it is expected that exports will be maintained at just under 4 million t/a. Poland's long-term position on the export market is assured providing that development at the Osiek mine to replace diminishing resources at Grzybow is carried out according to schedule. A major new sulphur source in the Communist World will come from the sulphur recovery from the sour natural gas fields in the Soviet Union, expected to commence this year. However, it is expected that the Soviet Union will use this new source to supplant imports from the Western World, and imports from Poland are expected to continue for logistical reasons. □



View of the Piaseczno mine where production began in 1957.

1966–1976 a period of growth

With the inauguration of these two mines the Polish sulphur industry entered a period of considerable growth in both production and exports. Capacity at Grzybow was raised to 1.2 million t/a, and subsequent investment in the Jeziorko mine raised capacity to 3.5 million t/a making it the largest sulphur mine in the world. Another open-pit mine at Machow began production in 1970 to replace capacity at Piaseczno which ceased production in 1971. However, output from Machow has been limited to less than 500,000 t/a due to technical problems and flooding. Problems at Machow were particularly severe in the period 1979–1981 when production was interrup-ted by a partial collapse of the overburden and flooding. As a result of new capacity at Grzybow and Jeziorko, Polish brimstone production grew tenfold during the lecade from 476,500 tonnes in 1966 to 4.9 million tonnes n 1976. The impact of these new sources of production on exports is evident from as early as 1967 when production from Grzybow was only on an experimental basis. Exports in 1967 reached 403,800 tonnes, an ncrease of 131,900 tonnes or 48.5% on the previous year. Polish sulphur exports continued to grow during the next lecade to reach 3.5 million tonnes in 1976, and secure Poland the position of the world's second largest sulphur xporter behind Canada.

As well as maintaining sales to its East European eighbours, the new production at Grzybow and eziorko enabled Poland to make inroads into other markets, particularly in Western Europe where Poland's competitiveness was aided by proximity to the markets and a freight advantage over other producers such as Canada. Among new markets for Polish sulphur were the United Kingdom, Greece, West Germany and France which have remained major customers. Markets were also opened in Tunisia and Morocco where Poland trades sulphur in exchange for phosphate rock as feedstock for the domestic fertilizer industry.

ie vat and spraying tower at Poland's largest sulphur mine at ziorko

The period 1966–1976 also saw a substantial increase in sulphur deliveries to the domestic market to provide feedstock for the rapidly expanding domestic fertilizer industry. Sulphur sales to the domestic market grew most rapidly between 1968 and 1974 increasing by 652,000 tonnes to 1 million tonnes. This leap in deliveries to the domestic market was due in particular to the inauguration of the massive Police fertilizer complex where around 1.3 million t/a of brimstone-based sulphuric acid capacity was brought on stream between 1969 and 1973.

The period from 1976 to 1984 witnessed a considerable slowdown in the growth of both production and exports from Poland. In marked contrast to the rapid expansion during the previous decade production remained around the 5 million t/a mark, and domestic sales also remained constant at just under 1 million t/a. Exports increased by only around 500,000 tonnes since 1976 to just over 4 million tonnes in 1984. Much of this increase can be attributed to an increase in exports to the USSR which grew by 352,100 tonnes, to 871,800 tonnes in 1984. This continued the trend of rapid growth in exports to the USSR, evident from the early 1970s, coinciding with a massive expansion in the Soviet fertilizer industry during the period. The USSR has thus become a net importer of sulphur, taking material from Canada and Mexico as well as Poland since 1980. As well as being the major external source of sulphur for the Soviet fertilizer industry, Poland was also the major supplier of technology, with the Polish engineering group Polimex supplying 51 sulphuric acid plants to the USSR since the initial requirement.

A slight downturn in Polish exports was witnessed in 1985, falling by 4% to 3.9 million tonnes. The main reason for this decline was bad weather during the first three months which adversely affected production causing a loss of 300,000 tonnes. Exports to Western Europe decreased by 7%, or 86,000 tonnes, and those to Africa were down by 32%, or 179,400 tonnes, as both

Iraq emerges as major sulphur exporter

With the initiation of large-scale sulphur production from one of the country's numerous sedimentary Miocene deposits and from the utilization of some of the oil-associated natural gas that was previously flared to waste, Iraq is beginning to realize its long-evident potential as a major supplier of brimstone to world markets.

The possible exploitation of these sulphur resources had been investigated as long ago as the mid-1930s, soon after Iraq became an independent state, and was in fact strongly recommended by a World Bank survey of the economy in 1951. However, it is only thanks to the Revolutionary Council of Ministers, who head the Baathist party which was returned to power after the Revolution of 17 July 1968, injecting a measure of political stability to the Iraqi economy that a firm and sustained commitment to these industrial projects has been made. Moreover, the establishment of the Frasch-type sulphur mine at Mishraq and of the gas desulphurization/sulphur recovery plant at Kirkuk was financed by Iraq itself.

Indeed, these two ventures are prominent features of the Government's much wider policy of using its oil revenues, boosted considerably in recent years by increasing State participation and higher posted prices, to bring about gradual industrialization of the Iraqi economy, based on its own natural resources.

The Ministry of Oil and Minerals was responsible for directing investment into both ventures. The administration of the Mishraq and Kirkuk complexes is handled by two separate branches of the Ministry, respectively National Iraqi Minerals Co. (NIMCO) and Iraq National Oil Co. (INOC).

Establishment of NIMCO

NIMCO was set up with an initial capital of ID 5 million ($15 million) in February 1969, only six months after the revolution that brought the present Baathist Government to power. One of the main articles of NIMCO's constitution is the exclusive right to mining concessions granted by the Government over all Iraqi territory for all minerals.

The establishment of NIMCO marked the end of a long series of negotiations with foreign interests anxious to exploit Iraqi sulphur resources.

During the early 1950s, for instance, Texasgulf Inc. registered an ID 1 million ($3 million) subsidiary company in Iraq and sought sulphur exploration and mining rights on Iraqi territory north of the 33rd parallel, offering to share profits from all mining ventures on a 50/50 basis with the Iraqi Government. In announcing the rejection of Texasgulf's bid in February 1954, the Iraqi Minister of the Economy stated: "The terms submitted by the company are inadequate to secure Iraq's full rights". One of the main stumbling blocks was Texasgulf's refusal to agree to the Government's call for a minimum production level of 500,000 t.p.a.

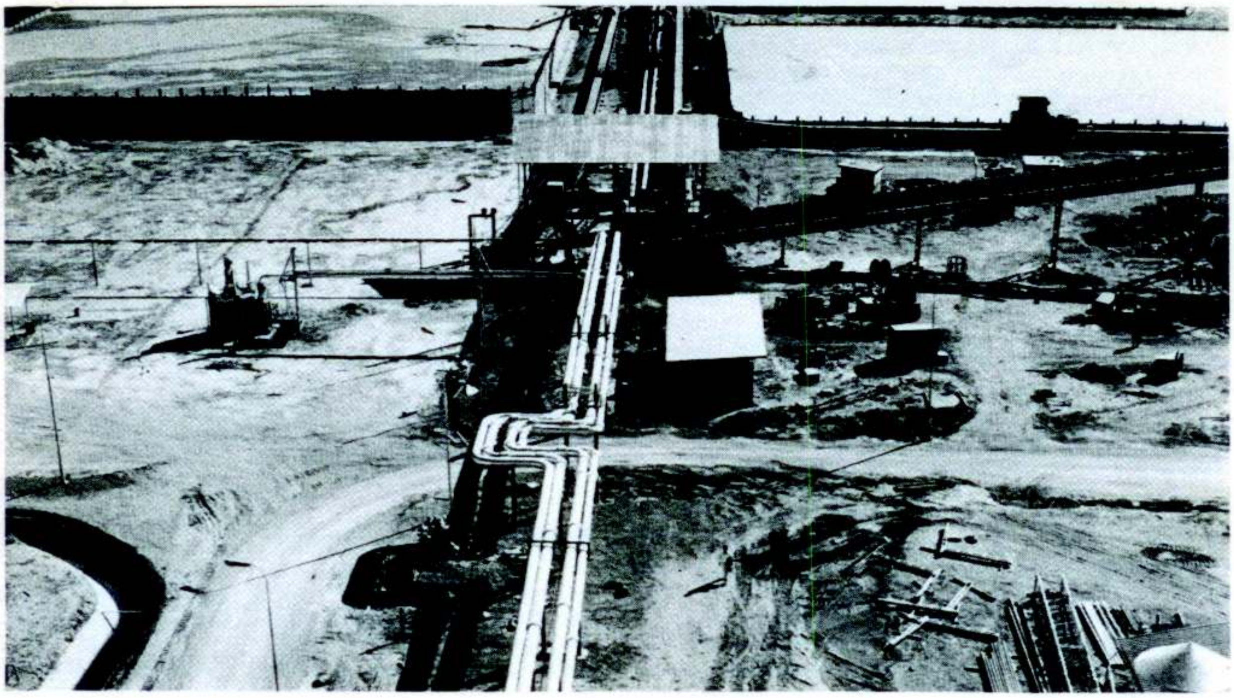
In 1961, Soviet geologists assisted the Iraqi Government in evaluating sulphur resources in the Al Fat'ha region of Kirkuk province but proposals for a Soviet-financed project to exploit these resources came to nought. Towards the end of 1966, the Iraqi Government issued a tender offering foreign participation in developing domestic sulphur resources but requiring the attainment of a brimstone production level of 1 million t.p.a. by 1972 and an investment of around $40 million to finance improvements in the related infrastructure, including the installation of a railway link to the mine, a power plant at the mine and the establishment of a new port at Umm Qasr. Sulphur producers from both France and the United States were attracted by this tender, but negotiations with them were abandoned by early 1968.

Meanwhile, in 1967, the Consultancy Division of The British Sulphur Corporation had completed a comprehensive geological, mining and marketing feasibility study on sulphur resources in northern Iraq.

Centrozap contract to assist in developing Mishraq

It was then decided that the Mishraq dome would be the best starting-point for a programme to develop Iraq's sulphur

It had once been thought that the occurrence of high bitumen concentrations in the Mishraq dome might well lower the quality of the sulphur product. However, thanks to the development of a new filtration process by Polish engineers, this problem has been resolved. Shown at left are the filtration facilities installed at Mishraq in 1972.



Vats at the Mishraq complex (shown here) can store up to 750,000 tons of solid sulphur. From the vats the sulphur is subsequently reclaimed and transported by rail to the port of Umm Qasr.

resources and in respect of the exploitation of the Mishraq dome a contract was signed at the end of May 1969 by NIMCO and Centrozap of Katowice, the Polish mining engineering institute. The hallmark of this agreement, as emphasized by Centrozap, was its recognition that the Mishraq mine, and all sulphur reserves and production associated with it would remain the inviolate property of Iraq.

Under the contract of May 1969, Centrozap agreed to provide mining engineering assistance in bringing on-flow a large new sulphur mine at Mishraq, on the bank of the River Tigris, near Mosul and about 400 km north of Baghdad. Centrozap and NIMCO intended to develop the mine in two stages, attaining a capacity of about 250,000 t.p.a. of elemental sulphur in the first stage, 1 million t.p.a. in the second stage. In addition to technical assistance, Centrozap agreed to supply, in collaboration with other Polish agencies, a large part of the necessary equipment and to train the Iraqi operating personnel.

The initial batches of Polish equipment for the Mishraq project were despatched from Kraków at the beginning of 1970 and in April of that year engineers from Hydrokop, the Polish mining construction organization, started to direct the drilling of boreholes into the Mishraq structure and the building of ancillary facilities, such as water-boilers, gathering stations, storage areas, etc.

First stage of Mishraq ready by start of 1972

By the end of 1971, Centrozap and Hydrokop had completed the first stage of the project. Trial production began in December 1971 and the Mishraq mine was officially opened amidst Army Day celebrations in Iraq on 6 January 1972. The second stage of the project, bringing capacity to 1 million t.p.a. was completed in the third quarter of this year.

Meanwhile, about 70 Iraqi engineers had been studying "underground-melting" techniques at the Grzybów and Jeziorko mines in Poland and Centrozap had arranged for on-the-spot training of about 780 Iraqi skilled workers at Mishraq. Like the Grzybów and Jeziorko mines of the Tarnobrzeg combine in Poland, which had themselves commenced production only as recently as the mid-1960s (see also *Sulphur* No. 78, September/October 1968, pages 10-14) the Mishraq mine was designed to use the "underground-melting" process. This process, which was originally developed by Ing. Bohdan Zakiewicz (Polish patent 57680) employs superheated water under pressure at a temperature of around 160°C for the *in situ* melting of sulphur in the sedimentary strata.

Another triumph achieved by Centrozap during the course of the Mishraq project was the development of a new process for the purification of dark sulphur. It had earlier been reckoned that the occurrence of very high bitumen concentrations in the Mishraq dome might well lower the quality of the sulphur product but the development of a new process by Prof. H. Leszczynska (patents pending) enables the bitumen content to be readily and easily filtered off prior to storage at the mine and onward transportation. The bitumen-removal unit at Mishraq was completed during the first quarter of 1972.

Also in connection with the system for purification of dark sulphur, NIMCO intends to install a small sulphuric acid plant at Mishraq; this corresponds to the facility installed at Jaltipan in Mexico during the early 1960s (see also *Sulphur* No. 23, October 1958, pages 34-36). In respect of the Mishraq project, Chemical Construction Co. (Chemico) secured in May 1973 a contract to engineer a 50 t.p.d. brimstone-based acid plant, costing some ID

250,000 ($625,000).

Furthermore, following the discovery of large bentonite deposits in northern Iraq, at Qara Tapa, where reserves were originally assessed at 500,000 tonnes, NIMCO has embarked upon the construction of a mill for processing this local bentonite. The material is to be used in the filtration system at Mishraq and will replace imported bentonite, saving the country some ID 1.5 million ($3.8 million).

Early in 1973 a Hungarian organization was awarded an ID 550,000 ($1.375 million) contract for supplying equipment designed to facilitate the storage and transportation of sulphur in liquid form.

At its Mishraq complex, NIMCO is also installing a small plant for producing ground sulphur, suitable for agricultural use.

Technical details of Mishraq mine complex

The Mishraq mine complex, which now has a capacity of 1 million t.p.a. comprises seven gathering stations, allied to 48 producing wells. Drilling of production wells and other wells is carried out by seven Failing 15005 rigs. Superheated water for "steaming" the dome is supplied from 16 boilers, each of them capable of providing 450,000 galls.p.d. In the initial stage of the project, from January 1972 until the third quarter of this year, the complex comprised four boilers serving two gathering stations, allied to 12 producing wells. There are also five steam generators and four air compressors supplying steam and compressed air to the mine. Until Mishraq was connected with the national power grid, power requirements were met by four electrical generators, with a total capacity of 5,850 kW; these facilities are now kept in stand-by condition.

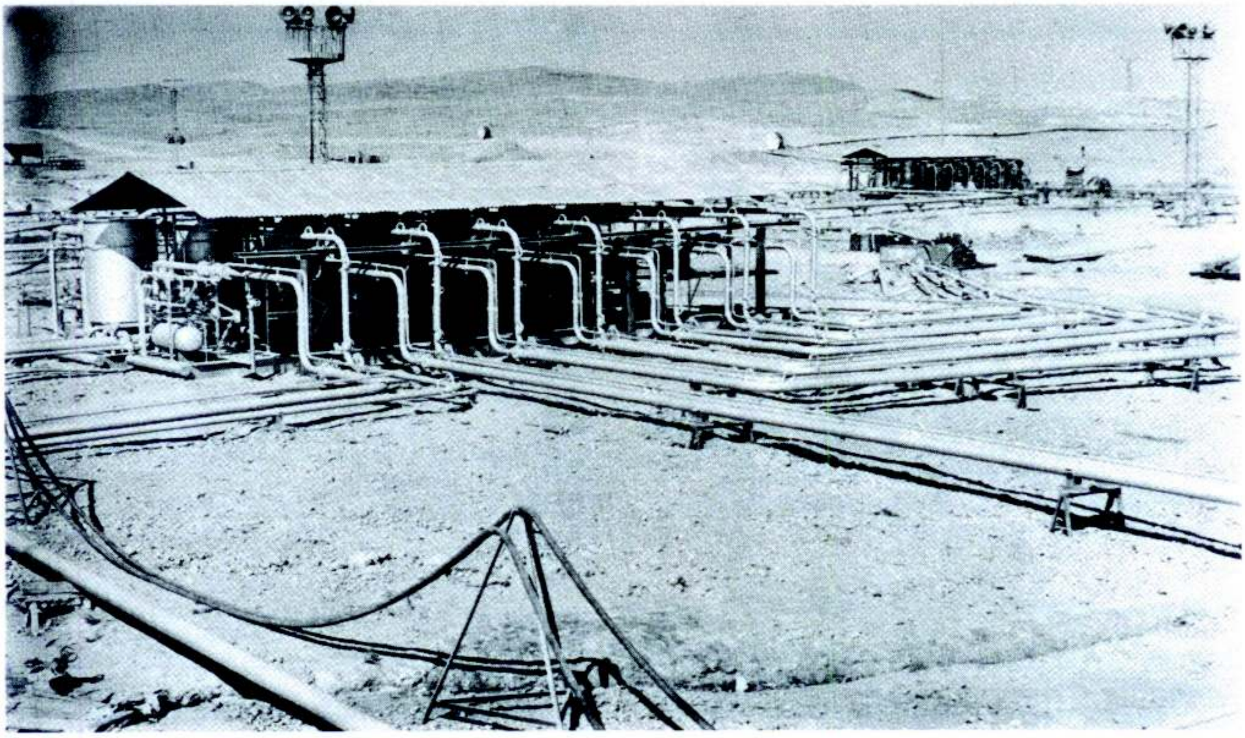
The critical factor determining operating costs in any Frasch-type mining venture is the water ratio, i.e. the quantity of hot water required to mine 1 tonne of sulphur; this factor sets the ceiling for the sulphur production rate that can be sustained from a given boiler plant. The water ratio itself is mainly determined by the physical characteristics of the deposit, notably its size and the porosity of the limestone formation in which the sulphur is contained, i.e. how much it "leaks". Also, because a large sulphur deposit, such as Mishraq, may take some years to "warm up", the water-ratio in the initial phases of operation is likely to be relatively high. For the Mishraq mine in full-scale production, NIMCO is basing its planned sulphur output on a water-ratio of 1,000-2,500 galls. per tonne sulphur.

The reasonably low water ratio, coupled with the availability of cheap and abundant natural gas from local sources, should guarantee very competitive sulphur production costs at Mishraq.

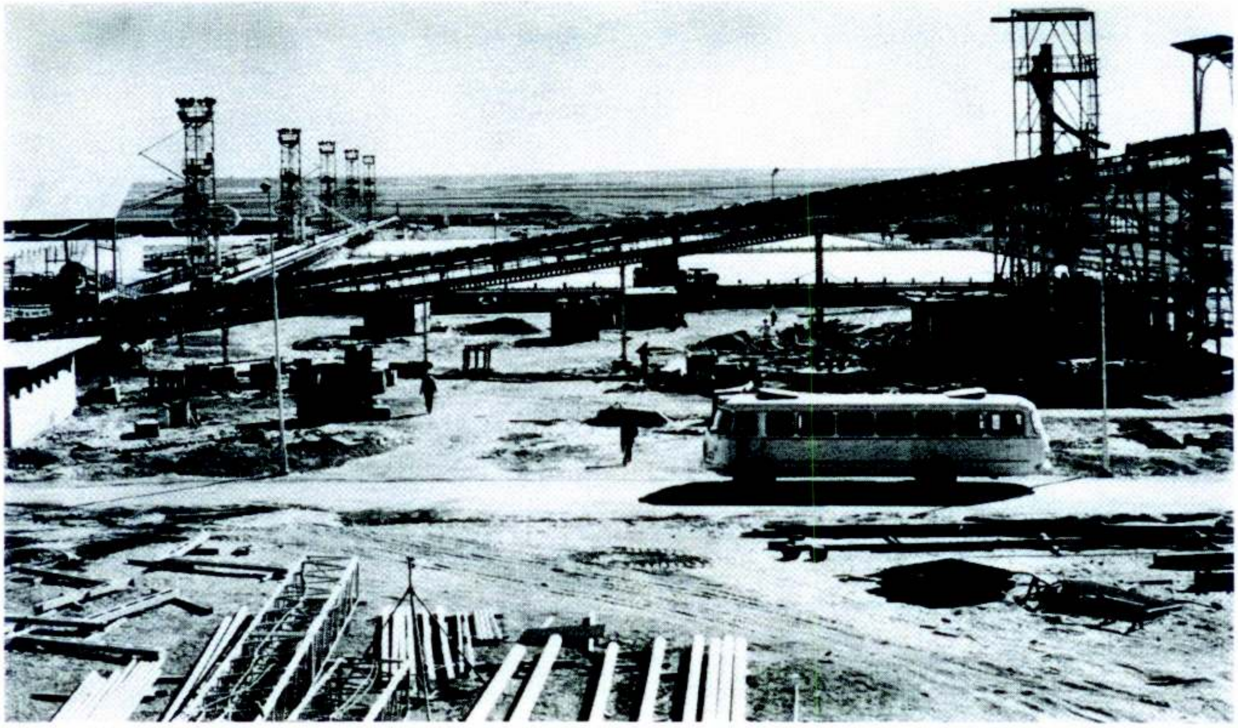
Rail and port facilities for sulphur exports

Storage facilities at the Mishraq complex comprise tanks for storing up to 13,000 tonnes of liquid sulphur and vats for storing up to 750,000 tonnes of solid sulphur. In the initial stage of operations, sulphur was being vatted at the mine prior to being loaded on to rail wagons destined for the port of Umm Qasr, about 900 km south of Mishraq.

Now that the second stage of the Mishraq project has been completed and 200 Polish-designed liquid sulphur rail cars are available, sulphur will be railed to Umm Qasr in liquid form, onwards from early 1975. It will be vatted at the port prior to crushing, retrieval and loading for export markets. Initially, vat storage capacity for sulphur at Umm



Key features of the Mishraq sulphur-mining venture are the production control stations (shown above). Here the flow of liquid sulphur from the dome to the processing plant is carefully monitored.



The design of the Mishraq complex incorporates 13,000 tonnes of liquid sulphur storage capacity and 750,000 tonnes of solid sulphur storage capacity. Shown here are facilities for storing and loading solid sulphur into rail wagons destined for the port of Umm Qasr, about 900 km south of Mishraq.

Qasr was 300,000 tonnes; this will be expanded at a later stage to 500,000 tonnes. Liquid sulphur storage capacity there will be 30,000 tonnes.

At the present time, Umm Qasr on the Arabian Gulf is the only port used by NIMCO for its sulphur exports. However, the Iraqi and Syrian authorities have been negotiating for some time a transit agreement, which would provide access to Syria's Mediterranean ports for certain Iraqi goods, including sulphur.

Utilization of oil-associated gas at Kirkuk

The second, albeit much smaller source of sulphur in Iraq, is the new gas-processing complex at Kirkuk, about 250 km north of Baghdad. The sulphur recovery plant here, which was finally commissioned in the second quarter of 1971, has capacity for producing 120,000 t.p.a. of sulphur. In addition, the complex includes a 250,000 t.p.a. LPG unit, connected to an 8 in. pipeline to Baghdad. Also, from the Kirkuk complex some 40 m.m.c.f.d. of desulphurized "clean" gas is supplied to the Al-Taji Gas Works in Baghdad via a 16 in. pipeline.

The main feedstock for the Kirkuk complex is natural gas from the local fields, worked by Iraq National Oil Co. The main feedstock contains 7-8% H_2S on average; this contrasts with the 13% originally anticipated. It is supplemented by 18-20% H_2S gas channelled to the desulphurizer from other processing plants.

As with the sedimentary sulphur deposits at Mishraq and elsewhere, the exploitation of oil-associated natural gas that has traditionally been flared to waste was strongly recommended by the World Bank survey of Iraq in 1951. Towards the end of 1956, the Iraqi Government Development Board approved the report of its industrial section on the feasibility of setting up a 275 t.p.d. sulphur recovery plant, costing an estimated ID 1.25 million (see also *Sulphur* No. 14, September 1956, page 39). At that time it was reckoned that throughout Iraq as a whole, around 100 m.m.c.f.d. of natural gas released during the working of crude oil deposits was being flared and wasted.

In 1959 Soviet consultants recommended Dibis, about 5 km from the Kirkuk oil fields, for the location of the proposed gas desulphurization sulphur recovery plant. The Ministry of Industry then appropriated an area of about 200,000 m^2 for the site of the proposed complex.

This was on the list of projects put out to international tender towards the end of 1963. In February 1965, Parsons-Power Gas Ltd., the joint venture set up by Ralph M. Parsons Co. of the United States and Power Gas Ltd. (now part of Davy-Powergas group) of the United Kingdom, was awarded an £8 million contract for the establishment of the Kirkuk complex. As well as design, equipment procurement, engineering and construction of the gas collection and desulphurization system, the sulphur recovery plant and the LPG unit, the Parsons-Power Gas contract of 1965 also provided for the building of administration and maintenance offices. Meanwhile, Sofregaz of Paris had been awarded a contract to install a 250 km pipeline from the site of the new Kirkuk complex to the Al-Taji gas works in Baghdad.

Construction work under the Parsons-Power Gas contract began early in 1966 and was completed the following year. However, technical problems, mainly centering on the compressor system and on the fact that the input gas stream was less rich in H_2S than had been originally anticipated, caused considerable start-up delays.

Trial production of sulphur at the Kirkuk complex eventually began in March 1971 and a few months later it was officially commissioned. However, continuing technical problems have handicapped operations at Kirkuk. The sulphur recovery sector yielded 35,000-36,000 tonnes in each of the years 1971 and 1972 – indicating a capacity utilization factor of less than 30%. Sulphur production at Kirkuk in 1973/74 to date indicates improvement.

The sulphur recovered at Kirkuk is vatted at the plant. Subsequent reclaiming involves the use of a *Trapcavator*-type shovel system. At the present time, some of the sulphur from Kirkuk is channelled to the newly established fertilizer complex at Basrah, but the major portion of the product should be available for export.

Domestic sulphur consumption

Naturally the existence of large domestic sources of sulphur should foster the development of sulphur-using industries in Iraq. For the time being, however, the country's brimstone consumption remains rather small.

Before the mid-1960s, less than 2,000 t.p.a. of brimstone was being consumed in Iraqi; the only end-use sectors being the agricultural industry and the oil refiners, using brimstone to enrich their sludge acid for regeneration and re-use. Then, in early 1968, National Rayon Co., established a rayon staple and fibres complex at Hindiyah, about 100 km south-south-west of Baghdad. Zahn & Co. GmbH of West Germany were responsible for engineering this complex. As part of it, a 3,000 t.p.a. carbon disulphide plant and a 12,000 t.p.a. sulphuric acid plant started up – both of them based on brimstone.

Much more important was the inauguration in July 1971 of the Abu Flus nitrogen fertilizer complex, near Basrah. Operated by the State Co. for Fertilizers, the contract for design and basic engineering for all units of this complex was awarded by the Ministry of Industry to Chemico; Mitsubishi Heavy Industries Ltd., was responsible for construction. The complex comprises facilities for producing 220 t.p.d. of ammonia, 175 t.p.d. of urea, 460 t.p.d. of ammonium sulphate and 360 t.p.d. of sulphuric acid; the latter unit is based entirely on brimstone and, working at full capacity, would account for some 40,000 t.p.a. of sulphur. The commissioning of the Abu Flus complex enabled the country to cease importing ammonium sulphate and to emerge as a net exporter of nitrogenous fertilizers. In mid-October this year, it was announced that Mitsubishi Heavy Industries had secured a $10 million contract to expand urea and ammonia capacity at Abu Flus by 1,000 t.p.d. and 1,200-1,400 t.p.d. respectively. Ammonium sulphate capacity and in turn potential sulphur consumption at Abu Flus will remain unchanged.

A much longer-term prospect for gradual industrialization based on increasing Iraqi sulphur consumption lies in the possible creation of a domestic phosphate fertilizer complex. Particular stimulus would be given to such a project if the phosphate rock resources of Iraq's western desert were to be developed. The Soviet Union has offered assistance for development of this area and it has been estimated that a 1 million t.p.a. mining operation could be comfortably sustained.

NIMCO's brimstone export programme

The creation and development of chemical and fertilizer industries in Iraq based on domestic sulphur resources has certainly been stimulated by the Mishraq and Kirkuk projects, but the main aim of these projects was always the generation of export revenue. Indeed, within a few years, sulphur will be second only to crude oil as the country's largest export commodity.

NIMCO is responsible for handling all sulphur exports from Iraq and during the past 2 years representatives of the organization have been actively negotiating sales contracts with customers throughout the world. In addition, sulphur has been specified among the list of commodities that can be exported from Iraq under the terms of barter agreements with a number of countries.

One of the most significant features of the initial NIMCO marketing programme is the agreement with Ciech-Siarkopol of Poland. Tentative arrangements for Polish assistance in marketing Iraqi sulphur had been mooted at the time the Centrozap contract for the development of Mishraq was signed (see also *Sulphur* No. 85, November/December 1969, page 49). Under the formal agreement, ratified on 18 February 1973, NIMCO sold 900,000 tonnes of brimstone to Ciech-Siarkopol. This entails 100,000 tonnes to be provided in 1973 and 200,000 tonnes to be provided in each subsequent year up to and including 1977. This material may well be used to meet Polish commitments in India and in penetrating other Asian and African markets.

Important sales contracts have also been made with India and with the People's Republic of China.

In September 1971, an Iraqi trade delegation signed the protocol for a 3-year barter agreement with India, providing for the export of sulphur and dates from Iraq in exchange for a wide range of engineering goods from India, including railway equipment and wagons for carrying bulk sulphur. Moreover, Iraq agreed to assist in financing the construction of a 2.5 million t.p.a. oil refinery in northeast India for which India agreed to purchase as feedstock Iraqi crude. The protocol was ratified in August 1972 and this year's entire contract tonnage of sulphur for India – 100,000 tonnes – had been shipped out of Umm Qasr by September. By 1975, brimstone deliveries from NIMCO to India should be running at 250,000 t.p.a.

Within the framework of the 1971 agreement between Iraq and the People's Republic of China to foster trade between the two countries, NIMCO signed a contract on 20 March 1973 to deliver 100,000 t.p.a. of brimstone to China over the next 5 years, effective as from August 1973.

In May 1973, NIMCO concluded a sale for 60,000 tonnes of brimstone to a Lebanese fertilizer company. In July, a small shipment of 7,000 tonnes was despatched to North Korea; this was a spot sale for the account of Korea Minerals Import & Export Organization. Additionally, 10,000 tonnes was contracted for export shipment in December 1973.

Consumers in other countries, notably Australia, Belgium, Chile, Egypt, Greece, Jordan, Pakistan, Taiwan and Tunisia, have also been seeking to take sulphur from NIMCO.

Thus, especially in the large brimstone markets of India and China, NIMCO of Iraq is emerging as a major competitor to Iranian and Canadian suppliers. The company is also well placed to encroach on these competitor's shares of the Southeast Asian, African and Australian markets. Moreover, when the Syrian/Iraqi rail links have been established – probably during the late 1970s – NIMCO should be better able to penetrate Mediterranean brimstone markets.

Frasch sulphur production down the years

By Bohdan Zakiewicz

Past, present – and future?

In this Anniversary issue of our journal we have devoted a considerable amount of space to consideration of the more significant events which have occurred in the world's sulphur industries during the past 25 years and to those likely to ensue in the next 25 years.

During the former period the importance of the Frasch sulphur industry – by which we mean, here, the brimstone mining industries of the United States and Mexico which are based on the ideas and techniques developed and put into practice by that German genius, Herman Frasch – which produced an average of 7.5 million t.p.a. for a total output of some 187 million tons during that period, is undeniable; as will be seen below, the senior, North American branch of the industry is at this moment in time in considerable danger of relatively imminent extinction, and its role and even its continued existence over the next 25 years will be largely dependent on decisions which the industry itself will have to make, very soon. The Mexican Frasch sulphur industry, though, is much younger than its counterpart across the border, and firmly based on reserves which, owing to the much lower price of natural gas in Mexico, probably exceed those still accessible to Frasch mining techniques in the United States. An adequate survey of both industries is not possible in a single article, and we have therefore deemed it desirable to review them in two parts, the first of which, hereunder, is devoted to Frasch sulphur production in the United States. Part 2, "Frasch Sulphur Production in Mexico", will be published in a future issue of our journal.

When Sulphur *first saw the light of day, however, the U.S. Frasch sulphur industry had already been in existence for 58 years, or almost 70% of its total life-span as of 31 December 1977, and it had, during that prior period, already produced well over one-third (38.6%) of its total output as of the latter date; indeed, it was in 1953, the year in which our first Bulletin was published, that the industry produced its 100 millionth ton! Under these circumstances, we cannot but begin this present survey of the industry by going a good deal further back into the past than the mere 25 years we are ourselves celebrating. Without those splendid books "The Stone that Burns" (D. Van Nostrand Co., Inc., 1948) and "Brimstone, the Stone that Burns" (ibid, 1959), by Williams Haynes, supplemented by the 3-part "Texas Gulf Story" published in Texasgulf Inc.'s house-journal, "Golden Triangle", we would be entirely unable to do so, and the writer is grateful for this opportunity to acknowledge his indebtedness to these sources of early data.*

PART 1. THE U.S. FRASCH SULPHUR INDUSTRY

The early years

It all began, of course, with Frasch himself. The presence of the sulphur in the caprock of the salt dome at the location now known as Sulphur Mine, in Calcasieu Parish, La., was first established as early as 1867, during the drilling of an exploratory oil well, and was soon confirmed by a number of additional wells. Around 450-650 ft deep, the sulphur-bearing formation was inaccessible to opencast working, and even if it had not been – as Frasch himself was quick to appreciate – the discrepancy between the wages paid to U.S. and Sicilian miners was such as to render this type of mining uneconomical in the United States in comparison with the much lower Sicilian costs; not one of the numerous attempts to gain access to the sulphur by conventional underground mining methods during the next 26 years was successful, either, and the presence of high concentrations of H_2S gas in the formation water, which caused the tragic deaths of 5 men in the course of one such attempt, strongly suggests that little if any of the 237.8 million tons of brimstone subsequently produced by the Frasch industry from this and similar deposits in the U.S. Gulf Coast region would ever have been won by those conventional methods.

Herman Frasch, born in Germany in 1851, emigrated to the United States at the age of 19; he rapidly became first interested and then expert in the fields of petroleum chemistry and chemical engineering – so expert, indeed, that within 6 years he was able to set himself up as a "consulting chemist specialising in petroleum and its products". In 1885, Haynes records, he bought the only Canadian petroleum producer then in existence, the Empire Oil Co., with wells and a small refinery in Ontario, which, when he purchased it, seemed doomed to failure because its main product, kerosene for lighting, had a foul smell and, when burned, left thick deposits of soot. Rightly suspecting that both were due to the presence of sulphur, Frasch succeeded, in less than a year, in developing a desulphurization process which produced an acceptable, saleable produce in place of what had hitherto been known, locally, as "skunk oil"!

Sour crudes in Indiana and Ohio were known to have similar characteristics, and John D. Rockefeller, with large holdings in one of the Ohio fields, bought up Frasch's Canadian company and patents outright, making Frasch the first director of research of the Standard Oil Co. Not long afterwards, treatment of these Midwestern oils by Frasch's desulphurization process raised their value from 14 cents to $1.00 a barrel!

Before he died, in 1914, Frasch was reaping the benefits of no fewer than 64 patents on his various inventions; these covered an amazingly wide field, embracing a broad spectrum of the chemical and metallurgical as well as petroleum industries. Concerning them, Haynes reported, in 1948: "Most were commercial successes: many of them involved huge operations. His discoveries in petroleum and sulphur .... have added billions to the world's wealth." Among them, of course, were the three sulphur mining patents he filed towards the end of 1890 embodying the basic principles on which Frasch sulphur mining was founded, which have, since Haynes wrote those words, added many more billions of dollars.

How Frasch first became interested in sulphur as a desirable, profitably-marketable commodity rather than as a deleterious, noxious component of certain hydrocarbon fuels is not on record, but once his attention became focussed on the problems besetting the would-be sulphur miners in Calcasieu Parish he was not slow to make use of the generous 2-months-a-year vacations to which he was entitled under his contract with Standard Oil, and it was only 4 years later that, on 28 December 1894, after 24 hours of steaming, the first brimstone ever to be produced by the Frasch method began to flow from the Sulphur, La., deposit, filling the 40 barrels provided to receive it in only 15 minutes and then overflowing into the first and probably the fastest-built sulphur vat ever constructed! Among the problems encountered during the next few months were, first, corrosion of the pump used to raise the molten sulphur, then, leakage of the mining water away from the production zone; to cure the first of these, Frasch turned to the now commonly used air-lift method of raising the sulphur, while he solved the second by another device which is also in common usage among present-day Frasch miners, comprising the injection of mud and chopped straw to block or impede the flow of the leaking water.

During these few months, the production of 500 or so tons of brimstone proved that his process worked, and ultimately led to the incorporation, on 23 January 1896, of his Union Sulphur Co., with the right to acquire title to the land, the mineral rights at Sulphur Mine and the Frasch sulphur patents.

The one problem to which Frasch was unable to find a solution was one that has become all too familiar to his successors today, namely the high cost of fuel! They had quickly exhausted all the wood available for miles around, and were compelled to turn to coal from Alabama, at a delivered cost of $4.50 per ton. It took about a ton of coal to melt and raise a ton of sulphur, and this high fuel cost, coupled with the cost of railing the sulphur produced all the way to New York and Boston, the principal brimstone-consuming centres of the time, not only caused the venture to lose money but also made it uncompetitive with cheap imported brimstone from Sicily; furthermore, with Union Sulphur in debt, Frasch was unable to bring into concurrent production enough wells to permit the continuous production, on a commercial scale, which might have made the operation a profitable one.

As it was, the sporadic production which took place during the last few years of the 1800s had only given rise to a few thousands of tons when, early in 1901, the situation was dramatically changed by the discovery of oil at the famous Spindletop gusher, only 60 miles distant from the mine. With unlimited quantities of oil available at 60 cents per barrel at the mine, it immediately became possible to bring more sulphur wells into production simultaneously: from 3,078 tons in 1901, output from Sulphur Mine jumped to 23,175 tons in 1903, then to 218,950 tons in 1905, and the infant Frasch sulphur industry was, at last, well and truly launched!

The Sulphur Mine was to continue in production until 1924. Meanwhile, though, as soon as it was seen to be successful, other producers began to appear – notably Freeport, in 1912, on Bryanmound, Tex., and, in 1919, Texas Gulf with its Old Gulf Mine on the Big Hill deposit. These two companies were to become the largest, most important producers in the industry, each securely based on really large, rich deposits as represented by Texas Gulf's Boling deposit,* which that company brought into production in 1929, and Freeport's Grande Ecaille (1933) and Grand Isle (1960) deposits, which have, between them, produced 55.6% of all the sulphur produced in the Gulf Coast region up to 31 December 1977. The other two company names which crop up most frequently in the annals of the Frasch sulphur industry are those of the Duval and Jefferson Lake Sulphur Companies, and it is only fitting that we should record, here, that the former, Duval, which now owns and operates what is currently the largest sulphur mine in the world – the Culberson or Rustler Heights mine, in Pecos County, West Texas – celebrates its 50th year as a sulphur producer in 1978, while Jefferson Lake, last year, had been producing sulphur for 45 years.

1952-1977: the good years – and the not so good years

The U.S. Gulf Coast region

As of 31 December 1952, the Frasch mines of the U.S. Gulf Coast region, which were still, at that time, the only mines of this type in operation, had already produced a total of 98.6 million tons of brimstone. At that moment in time, 12 different mining operations, on 9 different domes, had already come to an end; much of this tonnage had arisen from mines, started up prior to that date, which were still operating then; among the latter were Newgulf, Grande Ecaille, Orchard and Long Point, to name four of the more important, but Frasch's original Sulphur Mine, with 9.4 million tons, Freeport's Bryanmound with 5 million tons and Texas Gulf's Old Gulf Mine, with 12.35 million tons, had all contributed their quota and shut down prior to that date, as had Duval's and Jefferson Lake's smaller operations on Palangana and Boling in the first instance and Lake Peigneur and Jefferson Island in the latter.

Including the four mines already listed above, there were 10 pre-existing mines, operating on 10 different domes, still producing in 1953; with a little aid from Garden Island Bay and Damon Mound, which both started producing for the first time in November the same year, these mines produced almost 5.2 million tons in that year, lifting cumulative production of Frasch sulphur past the 100 million – ton

Frasch sulphur production down the years

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are subject to continuous transfusion by meteoric water. Furthermore, not only is gas consumption per ton of sulphur held constant throughout the life of the hydrodynamic mine, but the rate at which it is consumed is generally at so low a level that gas costs represent only a relatively minor fraction of the total operating costs, which are thus only marginally affected even by quite large increases in the price of gas.

The other principal difference between the two mining methods lies in the matter of reserves. The percentage of the geological reserves which can be recovered from a deposit being mined by the Frasch method is a variable figure determined by its unit gas consumption, gas prices and other operating costs vis-à-vis the price of sulphur, so that reserves decrease as costs rise unless there is an equivalent rise in the selling price of the sulphur produced. The constant, low gas consumption associated with the hydrodynamic method, on the other hand, coupled with the numerous other economies it now permits, ensures tha at least 85% of the geological reserves in the deposit will b recovered, making it possible to calculate recoverabl reserves before mining has even begun, in the certai knowledge that the figure arrived at will be recovered.

These two principal differences between the tw methods are, perhaps, best illustrated by the table overlea It presents a purely hypothetical situation in which it i assumed that 10 American mines are operating on deposit containing total geological reserves of sulphur of about 4 million tons, and presents figures which clearly illustrat the advantages of this method. It is especially noteworth that, whereas gas consumption on the existing Polish an Iraqi mines using it is around 5,000 ft^3/ton, it ha subsequently been modified and improved to the point a which a gas consumption of not more than 2,760 ft^3/to can now be guaranteed, affording the attractive possibilit of profitable mining even with gas costing as much a \$5.00/1,000 ft^3 instead of the \$2.00/1,000 ft^3 used in th table on page 68.

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Frasch sulphur production down the years

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Table
Comparison of Frasch and Hydrodynamic Mining, Gas and Reserves

	Frasch mining	Hydrodynamic mining
Geological Reserves tons $\times 10^6$	49	49
Recovery	55%	85%
Recoverable " " " "	26.95	41.65
Gas Consumption/tons $ft^3 \times 10^3$	9.92	2.76
Gas Cost/ton @ $2/$ft^3 \times 10^3$, $	19.84	5.52
Implementation of new technology, $/ton	–	0.60

The production of 41.65 million tons of sulphur by the hydrodynamic method represents a saving of 298 billion (10^9) ft^3 of gas, equivalent, at $2/$ft^3$, to $596 million or $14.3/ton. Assuming an at-mine value of $52/ton, furthermore, the additional 14.7 million tons of sulphur reserves produceable by the same method would be worth $738 million in additional sales. All this could be achieved at a cost of only 60 cents/ton, rather less than $9 million.

At present, the U.S. Frasch sulphur mining industry continues to operate as best it can under the difficult conditions now prevailing; there are 2 or 3 mines now producing which will probably be able to continue to do so for 10-20 years, the actual time during which they will stay in operation being dependent upon the extent to which they may be called upon to increase production, by installing additional plant capacity to replace the remaining mines as, one by one, the latter become compelled to close as costs rise to prohibitive levels. It will also depend on the rate at which natural gas prices continue to rise and, indeed, on the continued availability of natural gas itself. Should producers elect to pursue the Frasch method to the end, it is highly unlikely that, in 25 years time, there will be a single Frasch mine operating in the United States, and this once great industry may not even live to celebrate its Centenary! The wastage of gas, money and, above all, sulphur involved in the pursuance of such a course would, however, be appalling. The only alternative in sight at present would seem to be the general adoption of the hydrodynamic method by the industry.

The question then arises – are there sufficient reserves of sulphur left in the United States to support a revitalized Frasch industry adapted to hydrodynamic methods? At the outset, of course, the mines still operating would immediately be in a position to recover, on average, an additionally 30% of the geological reserves of sulphur in the deposits they were exploiting. In addition, there is not one abandoned Frasch mine in the country in which some geological reserves of sulphur are not still present, and although, in some of these mines, recoveries of more than 55% of the original *in situ* reserves may have been achieved, there are others in which recovery was much less and a few with almost all their initial reserves still intact. Assuming an overall recovery of 55% in the past, it can be calculated from the tonnage so far produced that, just in mines which have been exploited in the past, there are at least 107 million tons of sulphur remaining. Lastly, there are many deposits, in West Texas as well as the Gulf Coast, which, on investigation, were deemed to be unamenable to profitable exploitation by the Frasch method, and have never been mined; using the hydrodynamic method, on the other hand, many of them could be.

It is the present writer's considered opinion that, in all probability, taking all these potential resources into account, there are at least 200 million tons of profitably-mineable sulphur still lying beneath U.S. soil. The exact quantity will never be known until the last mine closes, of course, but there is certainly ample sulphur, and the requisite technology, available to carry the country comfortably through the otherwise crucial decade between 1980 and 1990, giving the recovery of sulphur from hydrocarbon fuels time to increase to the point at which the import of foreign sulphur, even from Mexico, will be unnecessary.

Otherwise, during the next 10 or 12 years, the ten Frasch mines now operating in Texas and Louisiana will all get older, and each, as the years go by, will be consuming more and more gas for every ton of sulphur it produces. Sharp increases in gas prices are likely during this period, and many of those mines will have to close as they become uncompetitive with imported recovered sulphur and cheap, hydrodynamically-mined sulphur from the vast deposits in Poland – so many, we believe, as to make it unlikely that U.S. Frasch sulphur production in 1990 will even approach the 5 million tons postulated in one recent forecast.§

The Frasch sulphur mining industry of the United States is, indeed, fast approaching a parting of the ways; the choice between death and rejuvenation is not a difficult one to make. Let us hope that it will be made in time to save some of the needlessly large quantities of badly needed natural gas and sulphur which will otherwise be wasted.

Footnotes

* See "Boling, the Sulphur Superdome", page 48, this issue.

† See *Sulphur* No. 122, January/February, 1976.

‡ See "Exploitation of Bedded Sulphur Deposits by the Hydrodynamic Method.", by B. Zakiewicz, *Sulphur* No. 120, September/October 1975.

§ See "A look at Sulphur – Today and Tomorrow", presented by Carmen P. Nelson, Freeport Minerals Co., at the AIME meeting, Denver, Colorado, 28 February 1978.