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AN INVESTIGATION OF INDUSTRIAL POSSIBILITIES OF OKLAHOMA GYPSUM AND ANHYDRITE

by

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ABSTRACT

Seven areas in Oklahoma are described in which commercial development of gypsum or anhydrite appears practical. Consideration is given to accessibility, transportation, fuel, and electric power sources.

A brief outline shows the current uses for gypsum and anhydrite, together with a review of the literature pertaining to possible uses for these materials in a manner other than presently employed in Oklahoma.

Results of laboratory experiments in the laboratory of the Oklahoma Geological Survey are shown which suggest a field for further investigation into industrial applications and uses for the tremendous reserves in Oklahoma of these naturally occurring calcium sulfates.

GYPSUM AND ANHYDRITE
in
OKLAHOMA

by
Albert L. Burwell

The gypsum deposits of Oklahoma are part of the Redbeds which are the surface rocks of the greater part of the western half of the State. The commercial deposits occur in two distinct geologic formations, designated as the Blaine and the Cloud Chief. The nature of the two formations will not be discussed at this time. Much of our present knowledge on these materials is based on Oklahoma Geological Survey, Bulletin 11, The Gypsum and Salt of Oklahoma, by L. C. Snider published in 1913 and now out of print. It is realized that some of the conclusions set out in this bulletin were drawn from erroneous information and care should be exercised in using the material.

The gypsum deposits of Oklahoma may be grouped for convenience into three regions: (1) the first line of gypsum hills along the Cimarron River, (2) the second line of gypsum hills running approximately 30 to 50 miles west of the first line, and (3) the Southwestern region, which is in the extreme southwestern part of the State.

The first line of hills are part of the Blaine formation, and there are three gypsum members of the formation throughout most of the range. The members are designated as the Ferguson, the Medicine Lodge, and the Shimer and are separated by beds of red and green shale. The outcrop is a pronounced eastward and northeastward-facing escarpment with soft red shale below. The outcrop enters the State from Kansas on the Salt Fork of the Arkansas River and follows down that stream for a few miles, swings back along the north bank of the Cimarron River, crosses the river near the Kansas line, and extends down the south side, gradually getting farther away from the stream until the gypsum hills die out in northern Canadian County.

The second line of hills is part of the Cloud Chief formation. The gypsum ledges appear in southern Woodward County and extend southward. Exposures occur in Dewey, eastern Ellis and Roger Mills, and in Washita, Caddo and Comanche counties. The ledges of this second line of hills are not continuous as they are in the first line. As a matter of fact, good exposures of commercial thickness and extent are rare. In the southernmost exposures they might be classed merely as outliers. Over most of the range the width of the gypsum belt is from five to thirty miles.

The Southwestern region gypsums occur in a manner similar to those of the first line of hills. Most of the commercial possibilities of the region are probably in the gypsums of the Blaine formation although there are good exposures in the Cloud Chief. Ledges of the Blaine formation extend from western Caddo County, westward across southern Washita and northern Kiowa counties, into south-central Beckham County, thence southward across Greer, Harmon, and Jackson counties to the Texas line.

A search for commercial quarry sites will involve several factors. Obviously, the list will include the thickness of the beds, the physical condition of the gypsum, the purity, the overburden, the dip and position relative to the surrounding terrain. It should include the availability of transportation, rail and highway, and of fuel and power.

In the following pages are set out descriptions of several areas wherein it would appear that ample quantities of gypsum are available and other conditions are favorable for commercial development.

AREA 1

This area is made up of a strip along the Cimarron River and Buffalo Creek, for a distance of approximately twenty miles, containing ample reserves of gypsum in workable ledges. The gypsum here is in the Blaine formation and much of it is coarsely crystalline selenite form. The eastern end of the strip is on the north side of the Cimarron River at a point near Fair Valley and extends to a little beyond Edith, thence westward across the river and up Buffalo Creek for perhaps five miles.

Gypsum of the Blaine formation exposed on the north side of the Cimarron River in the region from east of Fair Valley to a few miles east of Saratoga offers many possibilities. The bluffs are back from the river two to five miles. Several creeks enter the river at near right angles and each has cut a canyon or gully back into the gypsum upland. The canyon may be up to five miles in length and most are not over one half mile in width. This portion of the area lies in Woods County. Across the river near Edith, Buffalo Creek has cut a canyon in the gypsum about twelve miles in length and not exceeding one mile in width. This portion of the area is in Harper County.

The clearer exposures seem to show consistently three ledges of gypsum of which the lowest is the thickest, while the middle and upper ledges are of approximately equal thickness. The lower and middle ledges are separated by only a few feet of shale whereas the middle and upper are separated by an interval of some fifteen feet. A measured section in the W½ of section 24, Township 29 N., Range 17 W. found the upper (Shimer) ledge eroded, yet still eight feet thick. It is underlain in succession by twelve feet of shale, eight feet of middle (Medicine Lodge) ledge, seven feet of shale, and eighteen feet of the lower (Ferguson) ledge.

A branch of the A. T. & S. F. Railroad, operating west from Waynoka to Buffalo follows the Cimarron River on the north side from near Fair Valley to Edith where it crosses the river and follows Buffalo Creek to Buffalo. The railroad is relatively close to the gypsum ledges for twenty miles or more. The branch line joins the main line of the railroad at Waynoka, giving adequate service northeast and westward.

A high-pressure natural gas line of the Cities Service Gas Co. from the Panhandle gas fields passes near Buffalo and Alva on its way eastward. The distance from the ledges to the gas line is not great at any point. U. S. Highway 64 runs east and west just a short distance north of the gypsum ledges, the distance being just sufficient to clear the canyons which would require bridging. A paved spur runs south from the main highway to Freedom. A demand for electric power in this area would probably necessitate extension of power lines.

The reserves of gypsum in this area are large, - the tonnage is tremendous.

AREA 2

The second area is a portion of Woodward County where the A. T. & S. F. Railroad runs adjacent to Sand Creek and crosses the Cimarron River. This area lies mainly in Townships 23 and 24 N., Range 17 W. A measured section made on Sand Creek at a point five miles northeast of Quinlan has been reported:

Red clay with local deposits of gypsum	75 feet
Massive white gypsum (Shimer)	22 feet
Red clay	7 feet
Massive white gypsum (Medicine Lodge)	30 feet
Red clay down to creek bed	120 feet

It appears that the Ferguson member is absent in this area, as it is in several others.

Electric power is available by extension of lines from Waynoka. Natural gas service in the area is by Zenith Gas System, Incorporated. Oklahoma Highway 15 runs east and west through the area, just south of the railroad. There is sufficient gypsum in this area to take care of the needs of a large operation. A feature of the Medicine Lodge member in this area not found to the north is the appearance of anhydrite in the middle of the member.

AREA 3

The third area lies in Townships 18, 19, and 20 N., Range 12 W. which is in the south-central part of Major County and the northern part of Blaine County. At the northern end of the area the hills are rounded and inconspicuous but southward they are prominent and the canyons are steep sided. The gypsums in this area are fine-grained and dense, typical of "rock gypsum", whereas the gypsums in Areas 1 and 2 are the coarsely crystalline selenite form, a form that weathers more readily and produces a different topography.

In section 6, Township 20 N., Range 12 W., the Ferguson member is about 6 feet thick, and the Medicine Lodge at least 10 feet. The Shimer member is missing. Farther south in the SE¼ section 9, Township 19 N., Range 12 W., a measured section has been reported:

Gypsum (Medicine Lodge), top removed	4 feet
Anhydrite (Medicine Lodge)	3 feet
Gypsum (Medicine Lodge)	8.5 feet
Sandy shale and selenite bands	16.5 feet
Ferguson gypsum	6.5 feet
Greenish dolomitic sandstone	0.5 foot

About one mile farther southeast in section 16 the Medicine Lodge is at least 15 feet thick, the anhydrite portion being about 3 feet. The Shimer is 11 feet thick with the top removed. Farther to the southeast in section 26, the Ferguson is 8 to 10 feet thick. At this location the anhydrite portion of the Medicine Lodge member is 3 feet thick above which there is 10 feet of pure, fine-grained white gypsum.

The United States Gypsum Company has a plant at Southard in section 10, Township 18 N., Range 12 W., where the Shimer member is massive and fine-grained and 17 feet thick in places. In other places, however, the Shimer has been eroded away and the surface rock may be the anhydrite portion of the Medicine Lodge. To the north, in section 35, Township 19 N., Range 12 W., the S. A. Walton quarry furnishes gypsum, mainly for portland cement manufacture. To the south, west of the village of Ferguson, a measured section on the South Canyon of Salt Creek has been reported:

Massive white gypsum (Shimer)	15 feet
Soft, gray dolomitic sandstone	1 foot
Red gypsiferous clay	27 feet
Massive white gypsum (Medicine Lodge) (Anhydrite portion, 9 inches)	17 feet
Red clay with selenite bands	25 feet
Pinkish mottled gypsum (Ferguson)	4 feet
Red clay, banded with thin selenite	86 feet

Transportation in this area is supplied in the northern part by the A. T. & S. F. Railroad and in the southern part by the Frisco lines. State Highway 51 crosses the area from east to west. Electric power is supplied by the Oklahoma Gas and Electric Co. Natural gas is available from the Consolidated Gas Utilities Corporation whose high-pressure lines cross the area from southwest to northeast.

AREA 4

The fourth area might be called the Watonga area. It lies mostly in Townships 16 and 17 N., Range 11 W., and in Township 17 N., Range 12 W. A measured section in the SE¼ section 18, Township 17 N., Range 11 W., has been reported:

Shimer member, top eroded		14 feet
Red and green shale		32 feet
Medicine Lodge member,	gypsum	9 feet
	anhydrite	2 feet
	gypsum	6 feet
Red and green shale, with thin gypsum		32 feet
Ferguson gypsum		5 feet
Red shale		70 feet

About four miles southeast of this location, a section along the railroad shows 8 feet of Shimer, 12 feet of Medicine Lodge, and 3 feet of Ferguson. Continuing southeastward the gypsum beds gradually become thinner.

Railroad transportation in this area is by the Rock Island lines. The main highways are U. S. 270 and Oklahoma Highway 3. Electric service is by the Oklahoma Gas and Electric Co. The Consolidated Gas Utilities Corporation furnish natural gas. Universal Atlas Cement Co. operate a gypsum quarry in this area.

AREA 5

The fifth area is called the Weatherford area and lies mainly in Township 12 N., and Ranges 14 and 15 W. The hills that extend northwest from Weatherford to the west of Deer Creek and its tributaries contain ledges of gypsum up to 50 feet in thickness. Equally important beds are south and southwest of Weatherford. The gypsum varies in quality but the prevailing type is a fine-grained selenitic rock of white, pink, or red color.

Transportation is supplied by U. S. Highway 66 and by the Chicago, Rock Island and Pacific Railroad. Natural gas is available from the Consolidated Gas Utilities Corporation. Electric service is by the Public Service Co. The gypsum is in the Cloud Chief formation.

AREA 6

The sixth area lies south of Carter along the north bank of the North Fork of the Red River. The bluff where the M. K. & T. Railroad crosses the river offers excellent exposures. A measured section near this point has been reported:

Rough, weathered sandy dolomite capping the hills	3 feet
Red and green gypsiferous shale	24 feet
Massive white gypsum	23 feet
Red and green shale	6 feet
Massive white gypsum	18 feet
Red and green shale	15 feet
Massive white gypsum, occasional thin ledges sandstone	25 feet
Red and green shale	24 feet
Shale and gypsum bands	35 feet

This area is in proximity to one of Oklahoma's major natural gas fields. Service is supplied from lines of the Oklahoma Natural Gas Co. to the north and the lines of Consolidated Gas Utilities Corporation to the southwest. Oklahoma Highway 34 crosses the area from north to south, parallel much of the way with the Katy Railroad. Public Service Co. lines furnish electric power in this area. The gypsum is in the Blaine formation.

AREA 7

The seventh area is in the extreme southwestern part of the state. A report on the mineral resources of southwestern Jackson County was completed during September 1954 by M. E. McKinley and John H. Warren, geologists on the staff of the Oklahoma Geological Survey. This report has not been published but is on file at the offices of the Survey in Norman and open to inspection. Part of this report deals with the gypsum deposits near Eldorado, showing the location, the composition, and the estimated reserves. A plant was formerly operated at Eldorado by the United States Gypsum Co. who disposed of the property to the City of Eldorado who, in turn, have leased space to one or more industries.

This area is served by the Frisco Railroad and by Oklahoma Highway 44. Public Service Co. lines furnish electric power and Spearman Gas Co. distributes natural gas. The gypsum is in the Blaine formation.

OTHER AREAS

There are a number of other localities where the occurrence of gypsum should warrant investigation. The district south of Erick is one and the district west of Mangum is another. Older reports indicate that the Keechi Hills in Caddo County contain deposits of considerable magnitude. It has been suggested that there may be possibilities near Camargo in Dewey County. Sufficient information is not available on this location.

No attempt has been made to include gypsite occurrences in this review. The amount of gypsite is known to be great but the clay content is generally high, limiting its use to industry where the clay is not objectionable.

NATURAL CALCIUM SULFATE

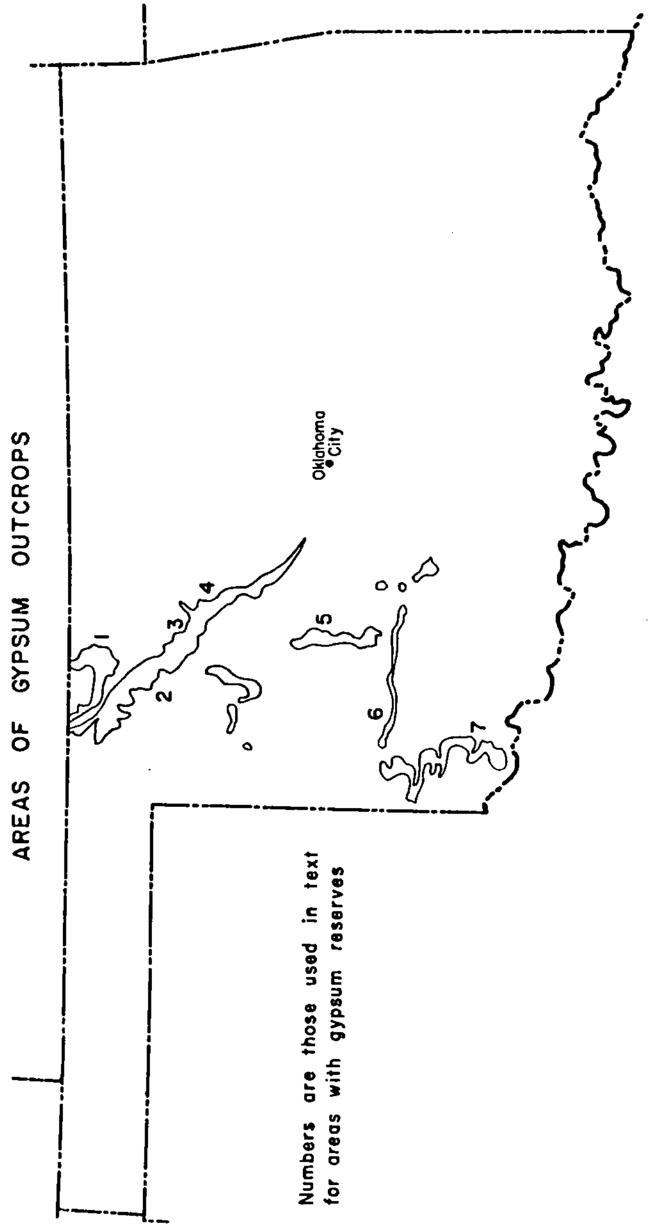
Calcium sulfate occurs naturally as gypsum, a hydrated compound whose composition conforms to the formula $CaSO_4.2H_2O$, and anhydrite, which as the name implies is free from water.

Gypsum is the name of a type rather than of a single mineral. Gypsum is found in several forms or varieties. One variety is known as selenite, a transparent, cleavable, normally colorless mineral. A second is satin spar, a fibrous form with a silky luster. A third is called alabaster, a massive fine-grained variety which is normally white and translucent. A fourth and commercially the most important is compact, granular, and coarser grained than the alabaster. The fifth is gypsite, an earthy, soft, impure material which is found in a noncoherent to slightly consolidated condition.

Gypsum is widely distributed throughout the world. It has served the human race in one way or another for thousands of years. Currently, the principal use is in the preparation of cementitious materials such as "plaster-of-paris" and wall plaster, materials which go into the manufacture of wall-board, stucco, structural blocks and forms. The raw rock is ground and is added to portland cement to control the setting. It is also applied to the soil to condition it for agricultural purposes and is then known as "land-plaster". Selected pure white rock is ground for "terra-alba" which is largely used as a filler in paper and in paint.

In Great Britain and on the continent of Europe, gypsum and anhydrite are the raw material from which sulfur dioxide, sulfuric acid, ammonium and magnesium sulfate are made. Economic conditions being different than in Europe, industry in the United States has not utilized these processes although conditions may change at any time.

AREAS OF GYPSUM OUTCROPS



Numbers are those used in text for areas with gypsum reserves

CONVERSION OF CALCIUM SULFATE
INTO
PRODUCTS OF GREATER COMMERCIAL VALUE

Extraction of sulfur from calcium sulfate by any of the known methods may not be economically feasible in the United States under present conditions. As long as elemental sulfur deposits are available for production by the Frasch process, new and less expensive means of utilizing the sulfur content of calcium sulfate must be found. The hunt for such means will continue as long as there are differences between production and consumption of sulfur and as long as transportation costs to points of consumption enter into industrial calculations. The situation in the sulfur market as of that date was set forth in the January 1952 issue of Chemical Engineering, pages 165 to 176, inclusive. The several sources from which sulfur and sulfur gases can be obtained are discussed together with the economics of such production. Among the sources from which sulfur may be recovered are sulfide ores such as pyrite and sphalerite, and also "sour" natural gas which contains hydrogen sulfide. Production and cost figures on the recovery from "sour" gas are given in the February 25, 1952 issue of the Oil & Gas Journal. Later information on the subject may be obtained from publications listed in the table of references.

The conversion of calcium sulfate, naturally occurring as gypsum or as anhydrite or byproduct material from industry, into other sulfur-containing products is being carried out in Great Britain and on the European continent. Two methods are currently in use, one involving the base exchange which takes place when calcium sulfate is agitated in a solution of ammonium carbonate to yield insoluble calcium carbonate and soluble ammonium sulfate, and the other involves the substitution of calcium sulfate for calcium carbonate in the manufacture of portland cement whereby the flue gases escaping from the kiln contain sulfur dioxide. These methods are not presently used in this country for economic reasons.

After consideration of such information as was available, the Oklahoma Geological Survey decided to undertake certain investigations into the possibilities with special reference to Oklahoma natural mineral resources and their utilization. This work has been divided into two parts. The first deals with conversion of calcium sulfate to ammonium sulfate and the second deals with thermal reduction of calcium sulfate. A discussion of each part follows.

CONVERSION OF CALCIUM SULFATE
TO AMMONIUM SULFATE

Ammonium sulfate is produced in the United States almost exclusively by absorption of ammonia gas in a solution of sulfuric acid, the ammonia being either synthetic or byproduct. In Great Britain and in Europe a substantial portion of the ammonium sulfate is produced by reacting ammonia and carbon dioxide with an aqueous suspension of calcium sulfate, which material may be natural or byproduct and either gypsum or anhydrite in composition. The reaction may be expressed by the formula:

$$2NH_3 + CO_2 + H_2O + CaSO_4 \rightarrow CaCO_3 \text{ (insoluble)} + (NH_4)_2SO_4 \text{ (soluble)}$$

The equation indicates a simple chemical change but when applied to commercial production the most complex chemical engineering difficulties are encountered. Large quantities of slurries have to be handled in the primary reaction itself, involving problems of stirring and prevention of settling, and during evaporation of the solution, after filtering, care must be taken to avoid discoloration. Another matter of concern is the crystal form of the product, which requires careful control of several factors. Since the reaction is reversible it is necessary that incoming liquor strong in ammonium carbonate shall not be immediately diluted with liquor containing very little ammonium carbonate. Therefore, elaborate equipment and a valve system is required. Further, reversibility of the reaction requires immediate removal of the calcium carbonate. The process, though old, has only recently been made commercially feasible.

The first attempt to apply this method to the production of ammonium sulfate followed the granting of French Patent 427,065 in 1910 and Addition 16,763 in 1912. German Patent 281,174 was issued in 1913 followed by 300,724 in 1916, 336,767 in 1919, and 383,004 in 1921[1]. Belgian Patent 446,274 was issued in 1943,[12] and British Patent 607,231 in 1948.[2] All these patents have one thing in common; that is, the reaction is carried out in aqueous media.[3,4,5,6,7,8,11,12]

Neumann[3] calculated the theoretical equilibrium factors and compared them with those found in actual trials. He used from 5 to 10 percent excess ammonium carbonate at several different concentrations on gypsum, hemihydrate, and anhydrite but never attained the theoretically possible yield of 99.95 percent. He obtained yield of 85 percent with gypsum, 92 percent with hemihydrate, and 90 percent with anhydrite. He attributed the low yield to the formation of the double salt $CaSO_4.(NH_4)_2SO_4$. He states that temperature exerts a negligible effect on the equilibrium. However, Teletov[9] and others investigated the effect of temperature and also of particle size and found it took 90 minutes to attain equilibrium at 20° C. but only 40 minutes at 50° C. but that grinding the calcium sulfate to below 40-70 mesh gave no advantage.

By 1932 the production of ammonium sulfate from gypsum in Europe had reached the stage where it was possible to make an economic survey of the several processes utilizing calcium sulfate and comparing them with the sulfuric acid absorption method.[10] The results show that in the Ukraine, ammonium sulfate from gypsum cost 12 to 20 percent less to manufacture and the capital investment required is 25 percent less than for the sulfuric acid absorption. In the United States the reverse of these figures were said to hold true, due without doubt to difference in cost of sulfuric acid, which stemmed from the availability of low-cost Frasch-mined sulfur from the Gulf Coast.

The techniques employed at the several European plants producing ammonium sulfate differ considerably. In some cases the reaction is conducted under pressure.[2,5,8] In one process the conversion is conducted in a saturated ammonium sulfate solution.[12] In another a tower is used and in others counter-current flow.[4,8] In general it appears that all operators endeavor to produce a pure crystalline ammonium sulfate. However, it is to be noted that in 1941 Claude [11] is credited with an improved process whereby "$CaCO_3$ and $(NH_4)_2SO_4$ are precipitated simultaneously in the ratio of 400 kilos $(NH_4)_2SO_4$ per ton" of the mixture and the product is "suitable for fertilizer". Claude suggests ways to enrich the sludge. He makes the statement that even with the calcium carbonate present as indicated there is not enough to compensate for the decalcifying action of the ammonium sulfate.

In all the literature and patents cited the reaction between calcium sulfate and ammonium carbonate is carried out in water, and water must later be removed from the product.

Experimental – Beginning in April 1951 experiments were undertaken in the laboratory of the Oklahoma Geological Survey and by September of that year it was discovered that it is possible to react calcium sulfate with ammonium carbonate, bicarbonate, or carbamate in the absence of added water. It was discovered, also, that gypsum, $CaSO_4.2H_2O$, can be reacted with gaseous ammonia and carbon dioxide in the absence of added water. Through the use of these discoveries many of the difficulties inherent in the previously known methods were eliminated. The product, whether the starting material is an ammonium carbonate or the two essential gases, is a dry and intimate mixture of ammonium sulfate and calcium carbonate. No attempt will be made

here to describe the several modifications of the process, but an example will illustrate the general idea.

If dry calcium sulfate be mixed with dry ammonium carbonate in equi-molecular proportions and the mixture confined in a closed vessel at room temperature there will be no perceptible change even after several weeks of intimate contact, but if the temperature be raised above the dissociation temperature of the ammonium carbonate a reaction takes place. The dissociation temperatures of the several ammonium carbonates and carbamates lie in the range between 38° and 60° C., whereas the dissociation temperature of ammonium sulfate is 100° C. With this knowledge, equi-molecular proportions of gypsum and ammonium bicarbonate were mixed and placed in a vessel on which a slight back-pressure could be maintained. The temperature was raised to 85° C. and held for 5 hours. The lid was removed and the contents exposed to the atmosphere at 85° C. until free moisture was expelled. Unreacted ammonium carbonate would also be expelled under these conditions. Analysis of the product indicated the composition as follows:

$$42.1\%\ CaCO_3 : 53.1\%\ (NH_4)_2SO_4 : 4.8\%\ CaSO_4.2H_2O$$

which represents a conversion of approximately 95 percent of the gypsum. It seems evident that moisture in the amount of two molecular proportions of water would be necessary if anhydrite were substituted for gypsum.

The product, being an intimate mixture of ammonium sulfate and calcium carbonate in dry powdered form, should offer possibilities as a new addition to the present list of nitrogenous fertilizer materials especially because of the control of soil acidity which accompanies the absorption of ammonia from ammonium sulfate by growing plants. Obviously, ammonium sulfate may be extracted and separated from the calcium carbonate if it is desired.

REDUCTION AND THERMAL DECOMPOSITION OF CALCIUM SULFATE

The basic factors involved in the decomposition of calcium sulfate have been known for years. Mendeleeff, in his "Principles of Chemistry" published prior to 1890, states that calcium sulfate may be converted to calcium sulfide by heating with charcoal. Thermal decomposition of calcium sulfate at high temperatures (about 1400° C.) is well known. Replacement of the sulfate radicle by the silica radicle is the basis for the production of portland cement from calcium sulfate and shale with recovery of sulfur dioxide as a byproduct at plants in Great Britain and on the European continent. Numerous persons in this and in foreign countries have investigated the possibilities of utilizing the sulfur content or the calcium content of calcium sulfate in one manner or another.[13,14,15] Some of the patents issued in this country are hereinafter reviewed briefly.

Baranoff and Hildt[16] describe a process using carbon to reduce calcium sulfate to yield mixed calcium sulfide and calcium carbonate from which hydrogen sulfide may be liberated by treatment with water. They react the hydrogen sulfide with more carbon dioxide to yield oxysulfide, which, in turn, is reacted with a further quantity of calcium sulfate to yield sulfur dioxide and elemental sulfur. It is stipulated that the reduction by carbon is carried out at "red heat" or below in order to inhibit as much as possible the formation of carbon monoxide. The patent makes use of several well-known reactions involving sulfates, sulfides, oxysulfides, and sulfur dioxide.

Bolle[17] proposes to reduce sulfates with "reducing gases" after mixing with certain metallic oxides which serve as catalysts. He states that steam will serve in place of the catalysts but does not include it in his claims, which pertain to the manufacture of alkali and alkaline-earth sulfides.

Roth and Brenek[18] describe a process for the "transformation of gypsum". Silica is used to replace the sulfate radicle. The products are calcium silicate and sulfur dioxide, obtained through the presence of steam and a temperature above 1100° C.

Hasselback[19] offers another replacement-by-silica process in which a mixture of gypsum, clay, and carbon is heated after casting in shapes or forms, and designed to prevent formation of sulfides.

Fleck[20] received a patent on a process for the manufacture of sulfur dioxide and quicklime. He states "we have now found that quicklime and sulfur dioxide can readily be obtained from calcium sulfate without the admixture of carbon and without the production of calcium sulfide, by directly heating the material with a reducing gas flame at temperatures between 1050° and 1300° C. Thus, gypsum or anhydrite may be fed into a rotary kiln in the interior of which a reducing-gas flame is maintained by admitting an insufficient amount of air for its complete combustion." His claims cover the production of quicklime and sulfur dioxide from calcium sulfate or mixtures of calcium sulfate and calcium carbonate in a reducing flame at 1150° to 1250° C.

Merriam[21] proposes to produce elemental sulfur from sulfur dioxide by using only such quantity of reducing agents as is necessary to effect the reduction. He states that hydrogen sulfide may be produced by similar means. In either case the reduction is on "gas mixtures containing sulfur dioxide and oxidizing gases".

Zirngibl[22] discloses a process the purpose of which is to produce alkali or alkaline-earth sulfides from the corresponding sulfate by reduction in the presence of a catalytic agent by reducing gases. The catalyst may be one of several oxides or oxide mixtures. The mixture of sulfate and catalyst is briquetted and subjected to reduction for upwards of two hours.

In another patent Zirngibl[23] reduces kieserite, a magnesium sulfate, to magnesia and hydrogen sulfide. The reducing agent is hydrogen which is "kept in circulation, at least ten times the theoretically-necessary quantity" at a temperature of 700° C. for two hours in the presence of a catalyst which may be iron, copper, molybdenum, or tungsten. The product is claimed to be "a pure magnesium oxide, hydrogen sulfide, or pure sulfur in a single stage process". Just how he obtains a pure magnesia after adding a metallic oxide is not explained.

DeJahn[24] developed a process for decomposing calcium sulfate to yield calcium oxide and sulfur dioxide. The ratio of gypsum to carbon is closely controlled, limiting the carbon per mol of calcium sulfate to 0.55 to 0.7.

Zirngibl[25] also holds a patent for the production of portland cement and sulfur dioxide from calcium sulfate, using a rotary kiln. He proposes that several reaction zones be maintained in which different temperatures and different atmospheres may be controlled.

Horn[26] proposes a process that is designed to yield calcium oxide substantially free from sulfur "without close control of the temperature or the use of special inert atmospheres...." The process involves heating "a finely divided mixture of calcium sulfate and elemental sulfur or a sulfide readily decomposable by heat.....to a temperature of about 2100° F. in the presence of an excess of air.....".

Advantage has been taken of the known reaction between hydrogen sulfide and sulfur dioxide to produce elemental sulfur. With hydrogen sulfide as starting material, a portion is burned to sulfur dioxide which is then mixed with more hydrogen sulfide. The two are reacted under proper conditions to yield elemental sulfur.

$$H_2S+3O \rightarrow H_2O+SO_2 \qquad SO_2+2H_2S \rightarrow 2H_2O+3S$$

Experimental. The problem of decomposing calcium sulfate into calcium oxide or other calcium compounds of satisfactory purity and acceptable physical properties from a commercial standpoint, presently or in the future, will necessarily be coupled to the recovery of the sulfur content of the calcium sulfate because of health, nuisance, or economic reasons. If the byproduct, containing the sulfur, is a mixture of sulfur compounds and other matter it must be susceptible to separation into components commercially valuable or readily disposable. The problem appears to have been solved in the manufacture of portland cement from calcium sulfate and argillaceous shale. The cement can be controlled to the desired sulfur residual and the byproduct gases can be processed to recover sulfur dioxide which may be converted to sulfuric acid. However, in the matter of producing a commercially acceptable quicklime or hydrated lime from calcium sulfate there are many unsolved problems. It is obvious that without recovery and marketing of sulfur or sulfur products, lime from calcium sulfate can not compete with lime produced from limestone. The fact that there are enormous deposits of gypsum and anhydrite (calcium sulfate) in Oklahoma and also ample supplies and reserves of fuel including petroleum, natural gas, and coal makes further investigation desirable on means of producing both lime and sulfur or sulfur derivatives from these naturally occurring materials.

Beginning in June 1951, experiments were started with the idea of reducing the sulfur in calcium sulfate to a gaseous form with a lower state of oxidation through the use of natural gas or of products derived from natural gas.

The first laboratory experiment was conducted using the following equipment: A reaction, condensing, and absorption train connected to a natural gas supply made up of a combustion-tube electric furnace with a Sillimanite tube of 1 inch diameter in which Sillimanite boats of proper size could be placed, and the tube coupled to a air-cooled condenser made of glass, followed by a water-cooled condenser, and then to a 500 ml. absorption flask, with an outlet to a flue. Glass traps were used with the air-cooled and water-cooled condensers to collect any condensate.

A boat was filled with granular gypsum and the absorption flask supplied with a solution of lead acetate made slightly acid with acetic acid. The system was checked for air-tightness, and natural gas passed until all air had been replaced. Then, and only then, heat was applied in the furnace and the temperature raised until products of decomposition made their appearance. A temperature of approximately 900° C. was maintained for a short time, the heat supply turned off, and natural gas flow continued until the system was again at room temperature. Examination disclosed that the boat and contents were heavily coated with carbon-black, the gypsum was altered and the resulting mass contained calcium sulfide, and that some hydrogen sulfide had

been collected by the absorber as shown by accumulation of lead sulfide.

A second experimental run was made exactly as in the first except that a bubble-flask containing warm water was introduced into the train ahead of the Sillimanite tube. This supplied some moisture to the natural gas. As a result less carbon was formed and more hydrogen sulfide passed to the absorber.

Further experimental runs were made in which the water in the bubble-flask was maintained at a boil or near the boiling point. This introduced a large excess of moisture and the results were considerably different. The gypsum was converted to calcium oxide relatively free from sulfide and free from carbon if sufficient time was given at the reaction temperature of 900° C. Considerable water and a small amount of elemental sulfur was condensed. The gaseous products were carbon dioxide, excess natural gas, and hydrogen sulfide.

The results of the experiments indicate clearly that the sulfur content of calcium sulfate may be extracted by processing the calcium sulfate with hydrocarbon gas, such as natural gas, with water vapor under controlled temperature, time of contact, rate of flow, proper proportions, and the right materials of construction.

Further work has been done on this method under the direction of the University of Oklahoma Research Institute through their contractural powers and with private financing. The objective of this has been and any future work no doubt will be to produce a quicklime or a calcium compound other than a sulfur derivative that will contain no impurity not already present in the original calcium sulfate and also to produce a recoverable sulfur or sulfur derivative in a form, concentration, and purity that will enable its use industrially. Just as in the processes involving the replacement of sulfur by silica where the economic feasibility of the method is due to the values of both solid and gaseous products, so comparable economic factors must be weighed in searching for other methods. On this basis the conversion of calcium sulfate by reducing with a mixture of natural gas and water vapor must yield a high-purity quicklime, hydrated lime, or equally acceptable calcium compound relatively free from sulfur compounds and free from metallic compounds such as would be present when metallic catalysts are employed. Further the sulfur should be in one form only so that its recovery and conversion to other forms may be accomplished readily and cheaply. It has been our objective to obtain a high-concentration hydrogen sulfide with as little free sulfur as possible. It is our expectation that the reaction of natural gas and water vapor on calcium sulfate when used in correct proportions, and with control of the temperature, rate of flow, time of contact, and with suitable materials of construction will yield the desired products at a cost competitive with similar products from other sources and by other methods.

SUMMARY

The existence of gypsum and anhydrite in Oklahoma in extremely large amounts and of high purity is known. Many occurrences are easily accessible, have adequate transportation facilities, low-cost fuel in close proximity, and can have electric power quickly where it is not already available.

Expansion in current uses of gypsum and gypsum products in Oklahoma depends entirely on expansion of markets for these materials. The experimental work outlined in this report suggests new commercial possibilities. Further work, especially on research and development pertaining to the engineering problems involved, will be necessary before these processes can be expected to be used commercially. In an area so largely agricultural the development of another nitrogenous fertilizer material for use in the area seems attractive, especially since the product overcomes one of the objections to the use of ammonium salts, that is, the residual acidity. The methods designed to yield lime and sulfur gas must be proven competitive with Frasch-mined elemental sulfur, a situation that depends upon the continued location of new sulfur-containing salt domes.

It is the purpose of this publication to call attention to Oklahoma's reserves of gypsum and anhydrite, and to encourage their further development and use. In order to protect the interest of the State all rights of the inventor (author) have been assigned to the University of Oklahoma Research Institute, which has legal right to accept patents and to negotiate with persons or companies desiring to develop and commercialize the processes.

LITERATURE AND PATENTS CITED

1. Industrial Chemicals. Faith, Keyes, and Clark. John Wiley and Son (1950).
2. Gordon, Kenneth and Imperial Chemical Industries, Ltd. British Patent 607,231, Ammonium Sulfate. Chem. Abst. 43:2380 (1949).
3. Neumann, B., Conversion of ammonium carbonate to ammonium sulfate with gypsum. Zeitschr. Angewandte Chemie (1921) Chem. Abst. 16:466 (1922).
4. Frydlender, J. H., Sulfuric acid and ammonium sulfate from calcium sulfate. Revue Produits Chimiques (1926) Chem. Abst. 21:476 (1927).
5. Baud, Paul, Manufacture of ammonium sulfate. Acad. Sci. Paris, Comptes Rendus (1927) Chem. Abst. 22:846 (1928).
6. Jackman, H. W., Ammonium sulfate. Gas Age Record 60:107-8 (1927) Chem. Abst. 22:1670 (1928).
7. Gallo, G., Chemical utilization of gypsum. Giornale Chimica Applicata (1927) Chem. Abst. 22:2442 (1928).
8. Wasillewski, L. et al., Ammonium sulfate from gypsum. Przemysl Chemizny (1930) Chem. Abst. 24:5942 (1930).
9. Teletov, I. S. et al., Reaction between calcium sulfate and ammonium carbonate. Ukrainian Khemichnii Zhurnal (1932) Chem. Abst. 27:2535 (1933)
10. Gasletius, G. I. et al., Economics of ammonium sulfate production. Ukrainian Khemichnii Zhurnal (1932) Chem. Abst. 27:2535 (1933).
11. Claude, George, Production of ammonium sulfate from gypsum. Acad. Sci. Paris, Comptes Rendus (1941) Chem. Abst. 37:2521 (1943)
12. Claude, George, Improvement in manufacture of ammonium sulfate. Belgian Patent 446,875 (1942) Chem. Abst. 41:6377 (1947).
13. Anhydrite fights Britain's sulfur shortage. Chemical Engineering, p. 212 (July 1951).
14. Shortage glamorizes gypsum. Chemical Engineering, p. 250 (Jan. 1952).
15. Stinson, J. M., and Mumma, C. E., Regeneration of sulfuric acid from byproduct calcium sulfate. Industrial Engineering Chemistry, p. 453 (Mar. 1954).

16. Baranoff, Valdimir de, and Hildt, Eugene, Process of obtaining sulfur from sulfates. U. S. Patent 61,639 (1898).

17. Bollo, Vittorio, and Cadenaccio, Ettore, Process for reduction of sulfates. U. S. Patent 1,045,769 (1912).

18. Rothe, Fritz, and Brenek, Hans, Process for transformation of gypsum. U. S. Patent 1,790,023 (1931).

19. Hasselbach, Alexander, Method of reducing gypsum. U. S. Patent 1,801,741 (1931).

20. Fleck, Alexander, Production of quicklime and sulfur dioxide. U. S. Patent 1,845,744 (1932).

21. Merriam, Henry F., Production of sulfur. U. S. Patent 1,919,342 (1933).

22. Zirngibl, Hans, Manufacture of sulfides. U. S. Patent 2,093,504 (1937).

23. Zirngibl, Hans, Process for reducing kieserite. U. S. Patent 2,171,966 (1939).

24. DeJahn, Frederik W., Process of decomposing calcium sulfate. U. S. Patent 2,232,099 (1941).

25. Zirngibl, Hans, and Strassen, Heinrick Zur, Manufacture of sulfur dioxide and portland cement from calcium sulfate and the usual additions containing aluminum silicates. U. S. Patent 2,252,279 (1941).

26. Horn, Knud, Reduction of sulfates. U. S. Patent 2,425,740 (1947).

OTHER PATENTS RELATED TO THE SUBJECT

Huber, Frederick W., and Poindexter, Robert W. Jr., Process of producing alkaline-earth-metal compounds. U. S. Patent 1,213,375 (1917).

Rosenstein, Ludwig, Recovery of sulfur. U. S. Patent 1,967,263 (1934).

Collier, Robert T., and Carriere, John G., Method of producing sulfur dioxide from waste acid-hydrocarbon containing material. U. S. Patent 2,435,710 (1948).

Meyer, Franz, Process of making sulfur dioxide. U. S. Patent 1,008,847 (1911).

Ikeda, Kikunae, Process of manufacturing hydrogen sulfide. U. S. Patent 1,351,755 (1920).

Caddick, Arthur James, Improvements in the production of ammonium sulfate from coke oven gas and other gases obtained from distillation of coal. British Patent 384,392 (1932).

Easterfield, Thomas Hill, Production of ammonium sulfate. U. S. Patent 1,072,840 (1913).

Vis, Gerhard Nicolaas, Process of manufacturing ammonium sulfate. U. S. Patent 1,152,244 (1915).

Vis, Gerhard Nicolaas, Process of obtaining ammonium sulfate. U. S. Patent 1,152,245 (1915).

Larsson, Markus, Method of producing ammonium sulfate. U. S. Patent 1,902,649 (1933).

Liljenroth, Franz G., Ammonium sulfate manufacture. U. S. Patent 1,758,449 (1930).