

benefit to the furnace operation, make possible the fixation and recovery of over 1 per cent of the air nitrogen.

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Analysis of Gypsum and Gypsum Products¹

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CALCIUM sulfate occurs in the natural state in two common forms, as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and as natural anhydrite (CaSO_4). It is also found sometimes as a double salt in several compounds, such as syngenite ($\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) and polyhalite ($2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum has many uses, anhydrite very few. As some anhydrite is usually contained in the gypsum, a satisfactory method of determining quantitatively the amounts of each present is necessary.

In the gypsum industry, however, there are four well-defined crystalline forms in which calcium sulfate is found: (1) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), (2) calcined gypsum or hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), (3) soluble anhydrite (CaSO_4), and (4) natural anhydrite (CaSO_4). Gypsum itself is used as land plaster and retarder in Portland cement. The hemihydrate, which is commonly called plaster of Paris, is made by calcining gypsum at about 140°C . This material is used in many ways, as wall plaster, molding plaster, etc. Soluble anhydrite, known as second settle stucco, is made by calcining gypsum at about 200°C ., but owing to its instability it must be used immediately after calcining. This product is sometimes used in making partition tile. Natural anhydrite takes up water very slowly to form gypsum and has very few uses at present. However, it is sometimes used as a filler in paints. A product similar to natural anhydrite may be prepared by heating gypsum at about 600°C . for several hours.²

These different forms may be distinguished microscopically,³ but no satisfactory method of chemical analysis has been developed that will determine how much of each form is present. The microscopic method, however, requires a knowledge of microscopic optical mineralogy which is not at the command of the ordinary chemist.

PRESENT METHOD OF ANALYSIS

The method in use at the present time for distinguishing the amounts of each constituent present is one recommended

Samples of raw gypsum were analyzed for gypsum and anhydrite according to present recommended method of analyses (Proc. Am. Soc. Testing Materials, 1921) and checked by microscopic analysis. The method was found to be unsatisfactory, variations of from 1 to 8 per cent occurring. The present method does not distinguish between the different forms that may be present: (1) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), (2) calcined gypsum ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), (3) soluble anhydrite (CaSO_4), and (4) natural anhydrite (CaSO_4). The following method is recommended which enables the chemist to determine the percentages of these constituents present in their mixtures: If gypsum, determine hygroscopic moisture by drying sample in air having a vapor pressure slightly greater than dissociation pressure of gypsum; then determine total combined water by drying at 200°C . If calcined gypsum, determine the total combined water as for gypsum and then pass air dried by 25 N sulfuric acid over sample to constant weight. From the total combined water, water taken up by sample from 25 N sulfuric acid to form $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and analysis for CaO and SO_3 , the amounts of gypsum, calcined gypsum, natural anhydrite, and soluble anhydrite may be calculated.

by the American Society for Testing Materials.⁴ It consists substantially in heating a thin layer of not less than 450 grams (about 1 pound) of the sample at 45°C . for 2 hours in order to drive off any hygroscopic moisture present (A. S. T. M. specifications for 1919 require that the hygroscopic moisture be driven off at 60°C .). One gram of the dried sample is then ground to pass a No. 100 sieve and heated in a covered crucible at 215° to 230°C . to constant weight in order to drive off the combined water. From the analysis of a sample for CaO, SO_3 , and combined water,

the amounts of gypsum and anhydrite are calculated.

The objections to this method are many:

1—From the vapor pressure curve of gypsum it will be seen that some of the combined water under some conditions would be driven off at either 45° or 60°C .⁵

2—Fine grinding of the gypsum is liable to cause serious error in the determination of combined water.⁶

3—The soluble anhydrite takes up water rapidly from air while being weighed in a crucible, and has a tendency to take up water from calcium chloride and sulfuric acid in a desiccator.

4—The results obtained do not show which constituents are present. For instance, in a mixture of gypsum, calcined gypsum, and natural anhydrite there is no way of telling in what combination the combined water is present, and accurate analyses are impossible.

SEARCH FOR IMPROVED METHOD

With these considerations in mind work was started on an improvement of the present method, or the development of a new method which would be accurate and would enable the chemist to distinguish between the four materials likely to be present. Samples of gypsum as fed to the calcining kettle were obtained from several manufacturers. These samples were screened and four different screenings obtained—on a No. 70, No. 70 to 100, No. 100 to 200, and past a No. 200 sieve. The amounts of gypsum and anhydrite present in each separated part and in the original sample were then

¹ *Proc. Am. Soc. Testing Materials*, **21**, 590 (1921).

² Received July 10, 1923. Published by permission of the Director, U. S. Bureau of Standards.

³ Stone, *Bur. Mines, Tech. Paper* **155** (1917).

⁴ *Proc. Am. Soc. Testing Materials*, **19**, Pt. 1, 617 (1919).

⁵ Calderon, *Bol. real. soc. esp. hist. nat.*, **11**, 756 (1911); *Z. Kryst. Mineralog.*, **54**, 200 (1914).

⁶ Steiger, *U. S. Geol. Survey, Bull.* **413**, 70 (1920); Hillebrand, *J. Am. Chem. Soc.*, **30**, 1120 (1908).

TABLE I—PERCENTAGES OF GYPSUM AND ANHYDRITE FOUND BY DIFFERENT METHODS
G = gypsum; A = anhydrite; O. S. = original sample before screening

GRAIN SIZE	Retained on Sieves Per cent	PRESENT						Microscopic A	Flotation A	New	
		Chem. I		Chem. II		Chem. III				G	A
		G	A	G	A	G	A				
Sample 1											
O. S.	..	69.7	3.5	70.2	3.5	74.3	0
On 70	6	52.0	8.0	62.9	0.0	59.3	2.5	0	..	63.0	0
70 to 100	3	55.0	8.5	65.0	1.0	0	..	64.9	0.6
100 to 200	10	54.0	8.0	68.5	0.7	64.2	4.0	0	..	66.8	1.8
Past 200	81	65.5	8.0	74.2	1.3	75.1	0.6
Sample 2											
O. S.	..	90.0	5.0	92.0	3.6	0	..	95.4	0.6
On 70	25	93.6	2.0	95.8	0.4	0	..	95.8	0.1
70 to 100	10	95.0	2.0	96.2	0.7	0	..	96.7	0.3
100 to 200	23	95.0	2.0	91.3	4.7	Trace	..	95.9	1.1
Past 200	42	91.0	4.0	97.5	3.0	0	..	96.3	0
Sample 3											
O. S.	..	63.7	8.0	67.0	5.5	7.2
On 70	5	74.3	12.0	73.4	13.0	7.0
70 to 100	6	78.4	12.0	79.4	11.0	5.0	81.5	6.3
100 to 200	21	63.6	9.5	69.0	5.3	7.1	7.0	85.2	6.9
Past 200	62	5.1	4.0	69.0	5.2
Sample 4											
O. S.	..	63.4	11.0	61.0	13.0	9.3
On 70	5	68.6	21.0	71.4	19.0	5.2
70 to 100	6	70.0	16.0	78.0	9.0	5.5	79.8	11.9
100 to 200	31	61.6	19.0	77.8	10.0	11.0	7.7	80.4	8.1
Past 200	58	8.0	7.0	75.4	8.0
Sample 5											
O. S.	..	63.8	8.6	65.2	7.5	71.4	1.8
On 70	4	36.4	2.1	34.4	3.0	37.6	1.1
70 to 100	2	48.2	2.4	46.7	3.7	0.3	..	49.9	1.1
100 to 200	8	58.5	3.9	59.3	11.0	2.3	60.9	2.1
Past 200	86	70.5	6.0	69.4	6.0	74.3	1.9
Sample 6											
O. S.	..	87.5	3.3	3.3	84.7	1.6
On 70	38	77.6	4.4	80.2	2.4	0.2	..	82.2	0
70 to 100	9	78.8	5.8	80.9	4.1	84.9	0.8
100 to 200	29	88.0	4.2	89.3	3.2	91.8	1.2
Past 200	24	81.6	4.1	79.9	5.4	84.0	2.1
Sample 7											
O. S.	..	91.0	6.0	94.8	3.0	2.0	..	97.1	1.5
On 70	21	90.1	6.8	90.2	6.7	96.5	1.8
70 to 100	9	92.4	5.6	93.5	4.7	98.7	0.6
100 to 200	23	92.2	5.6	95.7	3.0	98.3	0.8
Past 200	47	91.4	5.2	93.1	4.0	98.5	0
Sample 8											
O. S.	..	47.0	46.6
On 70	93.5	57.5	36.8
70 to 100	1.5	58.1	36.0	59.8	34.7
100 to 200	3	55.0	39.5	56.5	38.3
Past 200	2	62.1	33.5	61.2	34.3	63.8	32.3

determined according to the method of analysis at present in use. It was found that the percentage of anhydrite to gypsum was slightly greater in the coarse than in the fine material. The results of analyses are shown in Table I. Five chemists analyzed the samples and variations occur in every case.

In order to determine the accuracy of any method developed it was desirable to have some check on the results obtained. Therefore, the amount of anhydrite in each sample was determined microscopically by E. S. Larsen, of the U. S. Geological Survey. Although the analyses of different petrographers are subject to variations, the results should be quite accurate where the amount of the substance presence is quite small, as in the above case. The results of Larsen differed radically from those afforded by the chemical method described above.

Several methods for determining the amounts of gypsum and anhydrite in a sample containing only the two constituents might be suggested, one being a specific gravity method. However, this is not satisfactory, for gypsum always has impurities, such as calcium carbonate, silica, etc., incorporated with it. Determination by the relative solubilities was suggested, but was abandoned because the rates of solubility of the two materials are different,⁷ and because the size and shape of the particles affect the solubility.⁸

A flotation method was used with some success, but was abandoned because of the time required. In this method the two constituents were separated by bromoform, a liquid with a specific gravity between that of gypsum and that of an-

hydrite. Fair results were obtained with coarse particles, but great difficulty was obtained in getting an accurate separation of the fine particles.

Finally, a study of van't Hoff's vapor pressure curves of gypsum forming the hemihydrate, soluble anhydrite, and natural anhydrite was made. From these curves it would appear that the order of the transition of gypsum from one form to the other was reversed from the order obtained in actual practice.⁹

TABLE II—CHECKS OF GYPSUM IN SAMPLES

Obtained by analysis for total combined water and percentage of gypsum calculated from hemihydrate obtained by passing over the calcined sample air-dried by 25 N H₂SO₄.

Sample	Total Water Per cent	Gypsum Calculated Per cent	Water Taken up as Hemihydrate Per cent	Gypsum Calculated Per cent
1	17.64	84.4	4.45	85.1
2	17.67	84.6	4.39	84.7
3	20.10	96.0	5.2	99.4
4	20.75	96.8	5.11	97.6
5	14.80	70.8	3.77	72.1
6	10.90	52.2	2.70	52.4
7	12.85	61.5	3.30	63.5
8	13.30	63.6	3.28	62.8
9	15.95	76.3	3.92	75.3
10	18.10	86.6	4.67	89.0
11	20.20	96.0	5.01	96.3
12	12.00	57.5	2.98	57.3

The correctness of these curves, however, is questionable. Davis¹⁰ claims that curves for transition of gypsum to soluble anhydrite, and gypsum to natural anhydrite are incorrect. The writer's results, obtained by varying the vapor pressure over calcined gypsum, seem to justify Davis' criticism.

⁹ Van't Hoff, *Z. phys. Chem.*, **45**, 257 (1903).

¹⁰ "The Nature of the Changes Involved in the Production and Setting of Plaster of Paris," *J. Soc. Chem. Ind.*, **26**, 727 (1907).

⁷ McCaleb, *Am. Chem. J.*, **11**, 31 (1889).

⁸ Hulett, *Z. phys. Chem.*, **37**, 385 (1901).

It would seem that any hygroscopic moisture could be eliminated by passing over gypsum air which has a vapor pressure just above that of gypsum. In order to check this, samples of gypsum were exposed to a stream of air of a vapor pressure just above the dissociation pressure of the gypsum. These samples were then dried to constant weight. Samples immersed in

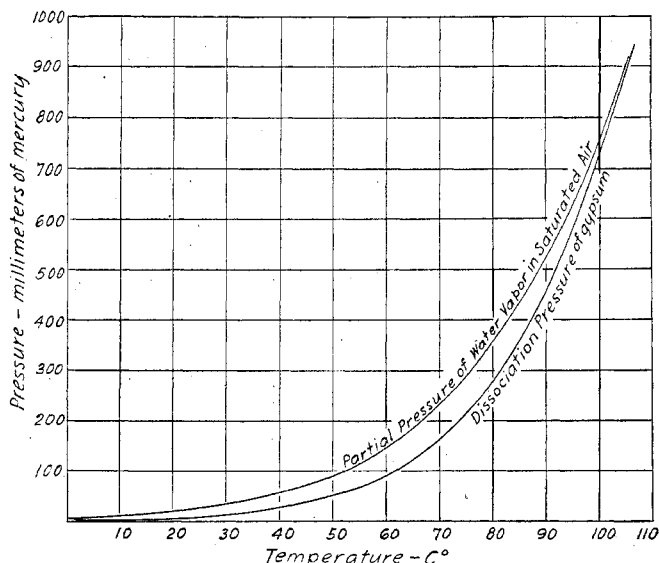


FIG. 1—DISSOCIATION PRESSURE OF GYPSUM

water were treated in like manner. Constant results were obtained. After removal of the hygroscopic moisture the samples were heated to constant weight in a U-tube at 200° C., and air-dried by passing through phosphorus pentoxide passed over the samples at the same time. The moisture driven off was collected in a sulfuric acid bulb. The loss in weight of the U-tube and the gain in weight of the sulfuric acid bulb served as a check. The water given off was combined water, from which the amount of gypsum in the sample was calculated. Samples analyzed in this manner checked more nearly the analyses by the microscope than did previous analyses.

Van't Hoff's curve for the dissociation pressure of gypsum to hemihydrate was assumed correct in this case. Further study of the curve made it seem possible that analysis of other forms of calcium sulfate could be made by varying the vapor pressure of air passed over gypsum. In an analysis of gypsum products there are five different phases to consider:

(1) H ₂ O Hygroscopic moisture	(2) CaSO ₄ ·2H ₂ O Gypsum	(3) CaSO ₄ · $\frac{1}{2}$ H ₂ O Calcined gypsum	(4) CaSO ₄ Soluble anhydrite	(5) CaSO ₄ Natural anhydrite
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The mixtures of these phases met with in practice would be: 1, 2, 5; 1, 2; 1, 5; 2, 3, 5; 2, 3; 2, 5; 3, 4, 5; 3, 4; 3, 5; 4, 5. It is not probable that any other mixture would exist except in a freshly calcined material, where gypsum, hemihydrate, and soluble anhydrite might be present. This combination is unstable and is not likely to be encountered.

As gypsum is unstable in the presence of air with a vapor pressure below that of gypsum, it is presumed that the hemihydrate is the stable form. On this assumption dehydrated samples resulting from the total water content determination as previously described were subjected to the action of a stream of air with a vapor pressure below that of the dissociation pressure of gypsum (according to van't Hoff's curve). The amount of water taken up by the soluble anhydrite should have been one-quarter of the total combined water, or about 6.6 per cent of the weight of the pure dry sample. However, such was not the case. There was a fairly rapid

rise in the amount of water taken up until 7 per cent was reached, then a more gradual rise. Van't Hoff holds that soluble anhydrite will unite with water when exposed to air to form exactly the hemihydrate (6.6 per cent H₂O). Cloez¹¹ and Gallo,¹² on the contrary, determined the amount of water absorbed by the anhydrite to be 8 per cent. Davis checked the work of Cloez and found that the soluble anhydrite in taking up the 8 per cent of water forms the hemihydrate and retains the excess as hygroscopic moisture. This combination is unstable and, from the hydrating property of the hemihydrate, does not seem possible.

TABLE III—RESULTS OBTAINED BY SUGGESTED METHOD ON MIXTURES OF CaSO₄·2H₂O AND CaSO₄· $\frac{1}{2}$ H₂O

Total Water Per cent	Water Taken up as Hemi- hydrate Per cent	CaSO ₄ ·2H ₂ O		CaSO ₄ · $\frac{1}{2}$ H ₂ O	
		Present Per cent	Found Per cent	Present Per cent	Found Per cent
10.16	3.86	40.1	40.2	28.4	28.6
10.44	3.83	42.2	42.2	24.4	26.2
11.20	5.65	35.8	35.4	62.3	61.4
11.25	3.51	49.1	49.3	16.1	15.3
10.05	3.94	38.9	39.1	31.3	30.1

As it seemed logical that there must be some point exactly at which the hemihydrate would be formed, the vapor pressure of the air was decreased until a point was reached at which the amount of water taken up by the soluble anhydrite was just one-quarter of the total combined water. This was obtained by passing the air over 25 N sulfuric acid. Several samples of gypsum were then calcined and the soluble anhydrite was treated in like manner. In each case the amount

¹¹ Bull. soc. chim., [3] 29, 169 (1903).

¹² Ann. soc. ing. arch. Ital., 27, Nos. 21 and 22 (1914); Gazz. chim. ital., 44, I, 497 (1914).

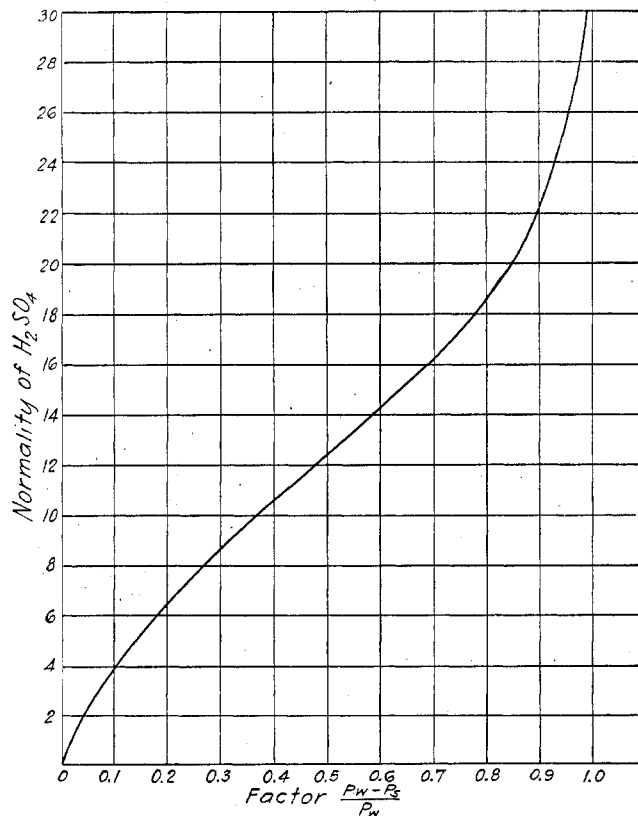


FIG. 2—VAPOR PRESSURE OF DIFFERENT AQUEOUS SOLUTIONS. [BOSWELL AND CANTELLO, Can. Chem. Met., 4, 109 (1920).] SULFURIC ACID CURVE Determination at 23° C. \approx 1°

$$\frac{P_w - P_s}{P_w} = \text{Relative dryness}$$

P_w = Vapor pressure of water
 P_s = Vapor pressure of solution

of water taken up was one-quarter of the weight lost on calcining. To samples of the hemihydrate obtained as above known amounts of gypsum were added, the mixtures were recalcined, and the total hemihydrate was obtained again. From the total water lost and the amount taken up again in forming hemihydrate, the amounts of gypsum and calcined gypsum could be calculated. The results obtained are shown in Table III.

It has been shown that the present analytical method for determining the amounts of the different phases of calcium sulfate present in a sample is very unsatisfactory. Probably the greatest errors come from fine grinding and the tendency of soluble anhydrite to form hemihydrate. From results of the analyses by the proposed method it appears that fine grinding of material is not necessary for accurate work. Determination by the microscope is a very satisfactory method, but as a chemical method is desirable the one described below is suggested.

PROPOSED METHOD

1—After grinding the sample until it all passes a No. 48 sieve, determine gravimetrically the CaO and SO_3 .

2—Decide from other evidence whether the sample is raw gypsum or calcined gypsum.

3—If raw gypsum, determine the hygroscopic moisture by drying to constant weight in a current of air having a vapor pressure slightly greater than the dissociation pressure of gypsum at the temperature of the experiment. The dissociation pressure of gypsum may be found from Fig. 1, and Fig. 2 shows the concentration of sulfuric acid necessary to give the air the desired humidity. These have been combined to make Fig. 3, which shows directly the concentration of acid required for any temperature. The loss of weight is reported as free water.

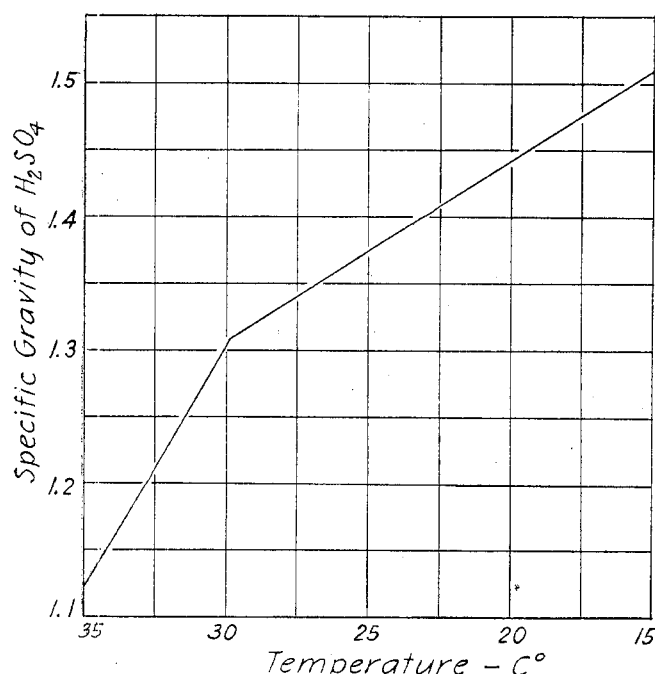


FIG. 3—CONCENTRATION OF H_2SO_4 AT $23^\circ\text{C} \pm 1^\circ$, THE VAPOR PRESSURE OF WHICH EQUALS THE DISSOCIATION PRESSURE OF GYPSUM BETWEEN 15° AND 35°C .

4—Complete the drying of the sample in a U-tube heated over a sand bath at 200°C . Pass a current of air, dried over concentrated sulfuric acid, over the sample, and absorb the water given off in concentrated sulfuric acid. Check the water thus collected against the loss in weight of the

sample. This is water combined as gypsum. Multiply this weight by $172/36$ (mol. wt. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ /mol. wt. $2\text{H}_2\text{O}$) and report as gypsum.

5—If the sample contains calcined gypsum, dry completely as in (4), and note the weight of water lost. Call this W . Cool the sample to room temperature and pass over it a current of air which has previously been passed over 25 N sulfuric acid. Continue this to constant weight and note the amount of water taken up. Call this w . The active part of the sample is now equivalent to calcined gypsum.

6—If $W = w$, the water lost and gained was all present in calcined gypsum. Multiply by $145/9$ (mol. wt. $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ /mol. wt. $\frac{1}{2}\text{H}_2\text{O}$) and report as such.

7—If W is greater than w , the sample contained both gypsum and calcined gypsum. From the molecular weights it is found that the amount of gypsum was $172/27 (W - w)$, and the amount of calcined gypsum was $145/27 (4w - W)$.

8—If W is less than w , the sample contained both calcined gypsum and soluble anhydrite. In this case all the water lost came from the calcined gypsum, which can therefore be found by multiplying W by $145/9$. $(w - W)$ represents the water taken up by the soluble anhydrite when changing to the hemihydrate. The soluble anhydrite is therefore found by multiplying $(w - W)$ by $136/9$.

9—Any CaO and SO_3 not accounted for above should be reported as natural anhydrite with the excess of either constituent.

The samples of gypsum tested were representative samples from the leading gypsum-producing sections of the United States, with the exception that no gypsites were analyzed. The effect of impurities in gypsite on the results obtained would be questionable. However, as some of the samples tested were quite impure, it is believed results just as accurate could be obtained with gypsites.

RESULTS

In Table I are given the amounts of gypsum and anhydrite found by the method recommended by the American Society for Testing Materials, the amount of anhydrite present according to microscopic analysis and to specific gravity separation, and the amounts of gypsum and anhydrite present according to the new method of analysis suggested. Table II gives the results obtained by analyzing at first for the water combined as gypsum and then forming the hemihydrate by passing air dried by 25 N sulfuric acid over the dried sample. Table III gives results of analyses of mixtures of gypsum and calcined gypsum.

ACKNOWLEDGMENT

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Extensive Use of Fertilizers

Among the concrete results of extension work along agricultural lines which the Department of Agriculture has been conducting may be mentioned increased interest on the part of farmers in the work with soils and in the use of commercial fertilizers. During the year 1922, 213,000 farmers consulted their county agricultural agents in regard to the use of commercial fertilizers. In addition, farmers conducted 15,235 fertilizer and 4035 lime demonstrations.

As a result of the activities in connection with lime, 48,000 farmers used 630,000 tons according to the methods advocated by the agents. In addition to the above, 105,000 farmers modified their methods of soil management. In order to maintain and improve soil conditions, 3750 drainage systems, involving 575,000 acres, and 29,000 pieces of terracing, involving 445,000 acres, were carried out according to the methods outlined by the extension workers of the Department of Agriculture.