

## STUDIES ON THE THERMAL DECOMPOSITION OF ALKALINE EARTH SULPHATES

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Decomposition of alkaline earth sulphates as such and in the presence of various substances has been studied. It was observed as follows: calcium sulphate decomposed 0.53% at 900°C. and 3.15% at 1050°C. maintained for 4 hours; barium sulphate 3.93% at 1050°C. maintained for 4 hours; strontium sulphate 0.82% at 900°C. and 5.164% at 1050°C. maintained for 4 hours; and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 43.0% at 900°C. for 6 hours.

The maximum decomposition of alkaline earth sulphates in the presence of alumina in the ratio of 1:1 by weight at a temperature of 900°C. maintained for 6 hours was noted to be  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 88% and  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , 9.72%, the water of crystallisation being subtracted in each case. These results differ a good deal from those presented by some of the previous workers.

Decomposition of alkaline earth sulphates in the presence of chromium oxide, chromite ore, kaolin, bentonites, calcined graphite (free of carbon) and various other oxides were tried, and it was observed that some form of silica accelerated the rate of decomposition. Diatomaceous earth, a form of amorphous silica, was also tried, and the results confirmed the above findings. As diatomaceous earth is not available in our country, 'flue dust', a source of active silica and an easily available raw-material, was substituted successfully. This process therefore can usefully be employed for the production of sulphur dioxide and the residue used in cement industry on commercial scale.

Gypsum is found in large deposits all over the mountain ranges in West Pakistan. At high temperatures<sup>2</sup> and under suitable conditions gypsum can be decomposed as follows:—



This reaction can be made use of in the decomposition of gypsum and other naturally occurring alkaline earth sulphates. But its industrial application would evidently depend on making the sulphates decompose at as low a temperature as possible and also as speedily and rapidly. Sulphur dioxide produced in the above reaction can be employed in various industrial processes.

The action of heat on gypsum has been studied by various workers from time to time during the last 30 years or so. Gervet<sup>3</sup> and his colleagues studied the effect of alumina on gypsum at 1400°C., Rana, Dube and Ratnam<sup>4</sup> studied the effect of temperature on gypsum and they obtained maximum production of sulphur dioxide upto 44.64%. Pailard et al.<sup>5</sup> studied the effect of kaolin on various sulphates for 6 hours in hydration, while Smirnov and Mehelov Patrosyan<sup>6</sup> studied the effect of heat on mixture of barium sulphate and alumina from 1200°C. to 1400°C., and the decomposition recorded by them was 40% and 93%, respectively, when the ratio was 1:1. Gruver<sup>7</sup> found the effect of heat on various sulphates on differential-thermal-analytical basis. Osmani and Datar<sup>8</sup> studied the effect of temperature on alkali metal sulphates in the presence of alumina and bauxite at 800°C. to 900°C. for 6 hours to get sulphur dioxide, and the same group of workers<sup>9</sup> also studied the effect of alumina and bauxite on alkaline earth sulphates. Suttén<sup>10</sup> and Manning and MacLennan<sup>11</sup> studied the effect of alumina, bauxite and silica etc. on gypsum at 900°C.

The present investigation was undertaken to study the action of heat on gypsum and other alkaline earth sulphates available in the country, with the object of decomposing them with various catalysts and other substances at as low a temperature as possible. For these studies, a thermogravimetric balance was designed so that more accurate observations could be made and a description of this instrument is also included.

### Experimental

The materials studied were magnesium sulphate, calcium sulphate, strontium sulphate and barium sulphate. All the sulphates used in the actual experiments were laboratory grade chemicals. However, to facilitate extension of the work to the naturally occurring minerals, analyses of gypsum, celestite and barytes were carried out with the results given below. Some of the available catalyzing minerals, bentonites, kaolin, chromite, graphite residue, diatomaceous earth and flue dust were also analysed for purity:—

1. Several samples of gypsum from Daudkhel were analysed and the average result is as follows: Free and combined water and loss on ignition, 25.366% (thermogravimetric balance);  $\text{CaSO}_4$ , 77.60%;  $\text{SiO}_2$ , 0.25%;  $\text{Fe}_2\text{O}_3$ , 0.07%; and  $\text{Al}_2\text{O}_3$ , 0.038%.

2. Only one sample of celestite from Daudkhel was analysed which gave the following results: Moisture and loss on ignition, 3.266% (thermogravimetric balance);  $\text{SrSO}_4$ , 80.30%;  $\text{SiO}_2$ , 11.0%; and  $\text{CaO}$ , 4.10%.

3. Average result given by the two samples of chromite ore is:—Moisture and loss on ignition, 4.290%;  $\text{SiO}_2$ , 11.0%;  $\text{Cr}_2\text{O}_3$ , 48.0%;  $\text{FeO}$ ,



13.70%; and  $\text{Fe}_2\text{O}_3$ , 6.12%.

4. A sample of barytes was also analysed which gave the following results:—Moisture and loss on ignition, 4.13%;  $\text{BaSO}_4$ , 73.2%;  $\text{SiO}_2$ , 12.9%; and  $\text{CaO}$ , 2.2%.

5. Nine samples of kaolin were analysed which gave the following average results:— $\text{SiO}_2$ , 45.17%;  $\text{Al}_2\text{O}_3$ , 38.25%;  $\text{Fe}_2\text{O}_3$ , 0.76%; and water content and loss on ignition, 14.9% (thermogravimetric balance).

6. Fourteen samples of bentonite gave the following average results:  $\text{SiO}_2$ , 53.96%;  $\text{Al}_2\text{O}_3$ , 10.36%;  $\text{Fe}_2\text{O}_3$ , 12.16%;  $\text{Na}_2\text{O}$ , 4.95%; and loss on ignition and water content, 15.9% (thermogravimetric balance).

7. Graphite residue was found to have the following composition:  $\text{SiO}_2$ , 80%;  $\text{Al}_2\text{O}_3$ , 11.2%; and  $\text{Fe}_2\text{O}_3$ , 5.5%.

8. Two samples of flue-dust from Daudkhel were analysed and were found to have the following composition:  $\text{SiO}_2$ , 50.5%;  $\text{R}_2\text{O}_3$ , 37.25%; and loss on ignition, 3.0%.

*Decomposition of Pure Sulphates.*—Sulphates with purity of E. Merck standard were used and the amount of water content was determined by two methods.

TABLE I

	(a) Heating & desiccating	(b) Thermogravimetrically
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	= 30.5 %	30.52 %
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	= 21.2 %	21.25 %
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	= 6.2 %	6.29 %
$\text{SrSO}_4$	= 0.5 %	0.55 %
$\text{BaSO}_4$	= 0.5 %	0.55 %
$\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	= 3.06 %	3.09 %

The requisite proportion of the components were weighed accurately and ground for 1-2 hours in an agate mortar. The sample was then transferred to a silica boat and reweighed. The decrease in weight varied from 9 mg.—15 mg. for each sample. This correction was made in the calculations.

The following heating arrangements were tried:—

- (1) Heating in Gallenkamp Global muffle furnace (0-1500°C.)
- (2) Laboratory muffle furnace (0-1000°C.)
- (3) Tube furnace (0-1100°C.). (Combustion nature).

Furnace (1) and (2) were later discarded due to some variations in temperature recorded with the help of the thermocouple-pyrometer arrangement. Furnace (3) of approximately 1" diameter was selected as it gave satisfactory results and so was used throughout the investigations. The furnace was equipped with a thermocouple pyrometer and a sunvic control. The samples were placed on the nickel half-round tube and introduced into the furnace and heated for a certain specified time at a fixed temperature. However the fluctuation was obvious which ranged  $\pm 10^\circ\text{C}$ . The samples were then taken out of the furnace, cooled in the desiccator and then weighed. The decrease in weight was recorded and the calculations were done on the basis of this decrease in weight, assuring it to be entirely due to decomposition. But as a cross-check the sulphate contents of the ignited samples were also determined gravimetrically. The results in both the cases showed close agreement. The decomposition of alkaline earth sulphates as such is given below:—

TABLE 2

Compound	Decomposition at			
	800°C.	900°C.	1000°C.	1050°C.
	(For 6 hours)			(4 hrs.)
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	6.802%	45.0%	100% in 45 minutes	—
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	nil	0.53%	2.52%	3.15%
$\text{SrSO}_4$	nil	0.82%	3.03%	4.16%
$\text{BaSO}_4$	nil	nil	2.6 %	3.93%

There were some differences between the above results and those of other authors,<sup>9</sup> which could not be entirely due to experimental error. In order to be more systematic and accurate a thermogravimetric balance, designed and fabricated by the authors as described below, was used.

*Thermogravimetric Balance.*—To study the minute changes on heating in the weight of substances, a thermogravimetric balance was devised by Honda and his coworkers<sup>13</sup> in 1915. Later on, Guichard and his colleagues,<sup>14</sup> Ghevenard and his associates in France, developed an automatic instrument of high precision and consequently a new technique of gravimetric analysis was introduced in the field of analytical chemistry.



As compared with Chavenard balance, a simple device was used by Burriel Mart; Barcia-Goyanes<sup>15</sup> at the University of Madrid. This consisted of a semimicrobalance in which one of the pans was replaced by a platinum crucible supported by a platinum wire. A thick layer of water separated the balance from the furnace. A sunvic control was used to regulate the temperature.

A similar set up with an analytical balance was used by the authors for the study of decomposition of alkaline earth sulphates. In the initial stages there were some difficulties which were mainly due to the following reasons:—

(1) The left pan of the balance was replaced by a platinum wire and a stationary counterpoise. This decreased the swing which resulted in continuous contact of the agate point and the lower agate plate, consequently increasing the stability and decreasing the sensitivity. (2) The beam was slightly

disturbed which resulted in erratic zero adjustment. (3) The platinum being a very good conductor of heat was affected even by the slightest variation in temperature, resulting in increase in the length of wire. (4) A thick layer of water was insufficient because it was heated after a few minutes which resulted in (a) disturbance in the level of the balance and (b) accumulation of water vapours in the balance.

In order to eliminate these defects, a modified thermogravimetric balance was devised by the authors for the determination of minute decreases in weight due to decomposition even at 1200°C.

Instead of replacing the pan by a platinum wire, contact of the platinum crucible was made through a hook attached at the base of the pan by a quartz fibre. This arrangement eliminated the above-mentioned defects (1) and (2), viz., restored the sensitivity of the balance without increasing

TABLE 3.—THERMAL DECOMPOSITION OF  $MgSO_4 \cdot 7H_2O$ \* (1 g. in each case) IN THE PRESENCE OF THE FOLLOWING SUBSTANCES WITH THE HELP OF THERMOGRAVIMETRIC BALANCE AT 900°C.

Reaction mixture	Ratio by weight	Moisture or water of hydration (mg.)	Decrease in mg. and % decomposition recorded after every hour												Total decomposition
			1		2		3		4		5		6		
			mg.	%	mg.	%	mg.	%	mg.	%	mg.	%	mg.	%	
$MgSO_4 \cdot 7H_2O$	1 : 0	302	54	11.7342	37	8.0401	36	7.8228	30	6.5190	26	5.6498	24	5.2152	44.9811%
$MgSO_4 \cdot 7H_2O$ + Alumina	1 : 1	336	130	28.249	63	13.6899	62	13.4726	62	13.4726	59	12.8207	55	12.6034	94.3182%
$MgSO_4 \cdot 7H_2O$ **	1 : 0	302	9	1.9557	5.8	1.2603	4.6	1.0001	4.4	.9126	4.2	9.126	4	.869	6.8072%
$MgSO_4 \cdot 7H_2O$ + Alumina**	1 : 1	336	62	13.4726	26	5.6498	20	4.346	20	4.346	19	4.1287	18	3.9114	35.8545%
$MgSO_4 \cdot 7H_2O$ + $Cr_2O_3$	10 : 1	302	80	17.384	54	11.7342	30	6.19	26	5.6498	24	5.215	22	4.7706	51.2726%
$MgSO_4 \cdot 7H_2O$ + $Cr_2O_3$	2 : 1	302	274	59.540	92	19.992	48	10.430	26.6	5.8902	16	3.4768	..	..	99.3290%
$MgSO_4 \cdot 7H_2O$ + Kaolin	10 : 1	306	106	23.0338	68	14.776	42	9.0266	36	7.8228	30	6.5190	30	6.519	67.6972%
„ „ „	2 : 1	388	186	40.7178	115	24.9895	54	11.7342	34	7.3882	22	4.7806	20	4.3460	93.9563%
$MgSO_4 \cdot 7H_2O$ + Graphite residue	10 : 1	302	95	20.6180	42	8.1170	35	7.5980	32	6.947	20	4.346	16	3.472	51.1457%
„ „ „	2 : 1	302	314	68.2320	72	15.6456	23	4.998	12	2.6076	10	2.1730	10	2.1730	95.8100%
$MgSO_4 \cdot 7H_2O$ + Chromite ore (ignited)	10 : 1	302	104	22.5992	68	14.7764	60	13.0380	48	10.4304	36	7.8228	32	6.9536	75.6804%
„ „ „	2 : 1	302	146	31.7258	106	23.0338	60	13.0380	39	8.4747	29	6.3017	24	6.2152	87.7882%

\*\* 800°C.

\* Decomposition of  $MgSO_4 \cdot 7H_2O$  (used) for a decrease of 1 mg. in weight= 0.2173%  
 „ „  $CaSO_4 \cdot \frac{1}{2}H_2O$  „ „ „ „ „ „ = 0.180 %  
 „ „  $CaSO_4 \cdot 2H_2O$  „ „ „ „ „ „ = 0.215 %  
 „ „  $SrSO_4$  „ „ „ „ „ „ = 0.232 %  
 „ „  $BaSO_4$  „ „ „ „ „ „ = 0.262 %



stability, and eliminated the error due to blunting of the knife edge and also the danger of disturbance of beam resulting in erratic zero. Use of quartz fibre eliminated defect (3), as the coefficient of expansion of quartz fibre is 0.256 as compared with 8.99 for the platinum<sup>17</sup>. Defect (4) was removed by a water circulating arrangement to maintain constant temperature throughout the experiment. In addition to the water circulating arrangement in the top of the chest, use of a water condenser was also made around the quartz fibre to minimise the heat radiations. Whatever little heat escaped to the balance was cut off by the arrangement made below the pan.<sup>18</sup> The whole of the heating arrangement was enclosed in a chest made up of iron and asbestos sheets fitted on a table made for the purpose. The chest had the sliding doors which after setting the balance to work, were closed to prevent any influence of outside air. A sunvic control was also used to regulate the temperature, which was measured with a thermocouple and pyrometer arrangement. A magnifier was also put before the scale on the door of the balance, to detect even the slightest variation in weight easily. Silica gel was also placed in the balance to prevent the effect of moisture, if any. Sensitivity of the balance was 0.0001 g.

Thermal decomposition of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in the presence of  $\text{Al}_2\text{O}_3$  and other tried substances as found by thermogravimetric balance is given in Table 3.

Since the above results showed that the findings of the authors<sup>9</sup> were not reproducible with the arrangements with us, efforts were made to select a suitable catalyst or a promoter to bring about the decomposition in reasonable time and at easily attainable temperature.

Data of decomposition of alkaline earth sulphate in the presence of  $\text{Al}_2\text{O}_3$ , chromite ore,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  etc. have been collected. The results of the above procedure though encouraging could not be taken as satisfactory. A major difficulty in the case of  $\text{Cr}_2\text{O}_3$  was when added more than 50% in alkaline earth sulphate attacked the glaze, and so that experiments were conducted using chromite ore, taking it to be commercially in this field. The results though encouraging could not be taken as satisfactory, as high temperature up to  $1050^\circ\text{C}$ . was used for 34.48% decomposition of  $\text{CaSO}_4$  in the ratio of 1:1 for 4 hours. The use of  $\text{Al}_2\text{O}_3$  is also a possibility, but as it is not available in sufficient quantity, kaolin (a hydrated alumino-silicate) was tried instead. The results are given in Table 3.

TABLE 4.—THERMAL DECOMPOSITION OF ALKALINE EARTH SULPHATES (1 g. in each case) IN THE PRESENCE OF DIATOMACEOUS EARTH WITH THE HELP OF THERMOGRAVIMETRIC BALANCE AT  $900^\circ\text{C}$ .

Reaction mixture	Ratio by weight	Moisture or water of hydration (mg.)	Decrease in mg. and % decomposition recorded after every hour												Total decom- position
			1		2		3		4		5		6		
			mg.	%	mg.	%	mg.	%	mg.	%	mg.	%	mg.	%	
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ + Diatomaceous earth	1 : 0.32	64	35	6.30	24	4.32	17	3.06	10	1.08	10	1.8	7	1.26	17.540 %
„ „ „	1 : 1	63.5	97	17.46	54	9.72	40	7.20	30	5.40	21	3.78	20	3.60	47.16 %
$\text{SrSO}_4$ + Diatomaceous earth	1 : 0.32	2.2	20	4.640	13	3.016	8	1.856	5	1.16	3	.696	2	.464	11.832 %
„ „ „	1 : 1	2.5	30	6.960	15	3.480	13	3.016	8	1.856	3	.696	2	.464	16.472 %
$\text{BaSO}_4$ + Diatomaceous earth	1 : 0.32	2.5	13	3.406	8	2.096	5	1.310	3	.786	3	.786	1.2	.3144	8.6984 %
„ „ „	1 : 1	2.5	24	6.288	15	3.930	10	2.620	5	1.310	3	.786	2	.534	15.368 %
$\text{MgSO}_4 \cdot x\text{H}_2\text{O}^*$ + Diatomaceous earth	1 : 0.32	305	198	93.0254	80	17.3840	63	13.6899	29	6.2717	19	4.1287	10	2.1730	86.6677 %
„ „ „	1 : 1	305	232	99.9136	128	27.8144	63	13.6899	30	6.5190	10	2.1730	2	.4346	100.0385 %
$\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ + Flue dust	1:0.32	305	81	17.6013	72	15.6356	54	11.7342	18	3.9114	13	2.8249	10	2.1730	53.8804 %
„ „ „	1 : 1	305	166	36.0718	76	16.5148	67	14.5391	58	12.6034	42	9.0636	30	6.5190	95.3217 %

\*at  $800^\circ\text{C}$ .



Since the results are definitely better than those of  $\text{Fe}_2\text{O}_3$ , chromite ore etc., other aluminosilicates were tried for further improvements. Second in order was bentonite (a montmorillonite structure). Another substance available known as graphite residue of the composition given earlier was also tried for the decomposition with the results shown in the table.

It was found from the above table that there was a marked increase in the decomposition of alkaline earth sulphates in the case. Since there was a large amount of silica and alumina and small amount of  $\text{Fe}_2\text{O}_3$  as compared with bentonites, it was necessary to find out which of the constituents contributes much in decomposition. For this purpose data were collected with mixture of  $\text{Fe}_2\text{O}_3$  plus kaolin and bentonites in the ratio of (0.1:1) at  $1050^\circ\text{C}$ . for 4 hours respectively. From the tables it was inferred that  $\text{Fe}_2\text{O}_3$  had little effect on the decomposition of alkaline earth sulphate. Data were also collected with mixture of alumina and kaolin and bentonite. It was further concluded that the presence of silica (amorphous) had much more tendency of decomposition of alkaline earth sulphate than alumina. So a form of amorphous silica, i.e., diatomaceous earth, was used for the decomposition.

Data have been obtained with the help of thermogravimetric balance for the decomposition of alkaline earth sulphates in the presence of diatomaceous earth at  $900^\circ\text{C}$ ., and the results are given in Table 4.

TABLE 5.—THERMAL DECOMPOSITION OF ALKALINE EARTH SULPHATES IN THE PRESENCE OF FLUE DUST.

Reaction mixture	Ratio by weight	Temp. $^\circ\text{C}$ .	Time	Decomposition %
CaSO <sub>4</sub> + Flue dust	1 : 0.32	900	6 hrs.	14.4
	1 : 0.5	"	"	16.8
	1 : 1	"	"	20.3
	1 : 0.32	1000	4 hrs	26.0
	1 : 0.5	"	"	32.7
	1 : 1	"	"	68.2
SrSO <sub>4</sub> + Flue dust	1 : 0.32	1050	"	38.8
	1 : 0.5	"	"	88.2
	1 : 2.32	1000	"	26.5
BaSO <sub>4</sub> + Flue dust	1 : 0.5	"	"	31.5
	1 : 0.32	"	"	24.03
MgSO <sub>4</sub> .7H <sub>2</sub> O + Flue dust	1 : 0.5	"	"	29.9
	1 : 0.32	800	6 hrs. } See Table 1	
"	1 : 0.5	"	" }	

As the diatomaceous earth is a rare substance it may not be possible to use it for decomposition on commercial basis. Another substance which is the flue-dust from the burning of indigenous coals of the composition given earlier was tried. The results obtained are given in the last two rows of Table 4 and in Table 5. The above results are most commendable for the utilization of alkaline earth sulphates on commercial basis at easily attainable temperature.

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