

STUDIES ON THE UTILIZATION OF "SPENT" OXIDE

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Utilization of "Spent" oxide—a waste product of the Fertilizer Factory, Daud Khel (West Pakistan), has been investigated. "Spent" oxide can be reactivated with 40 percent sodium hydroxide solution and on sintering with sodium carbonate (1:1 by weight) at 850°C.

Recovery of sulphur from "Spent" oxide by treatment with 5 percent of sulphuric acid solution yielded sulphur of 99.8 percent purity. 70 percent of total iron oxide present in "Spent" oxide is recoverable as hydrated iron oxide and sulphuric acid used originally is converted into ammonium sulphate, an important nitrogen fertilizer.

Introduction

The hydrated oxides of iron, both natural and synthetic, are used for removing hydrogen sulphide from coal gas, water gas and other fuel gases. M/S. Pak. American Fertilizers Ltd., Iskandarabad (West Pakistan) import large quantities of "Lux-masse" and Bog ore every year for purifying the sour water gas. The oxide after revivification and 3 successive foulings attains a sulphur content of 40 percent and is rejected as a waste. Thus the factory has the problem of the disposal of "Spent" oxide which has been accumulating over a period of several years. This investigation was undertaken to study the possibilities of profitable utilization of this waste. The studies reported in this paper were carried out from two different angles: (1) To study methods and conditions of reactivation of "Spent" oxide so that it could be reused for purification, and (2) To study the recovery of sulphur from "Spent" oxide.

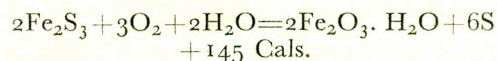
REACTIVATION OF "SPENT" OXIDE

Theory of Hydrogen Sulphide Absorption by Ferric Oxide.—The ferric oxide in a suitable form (usually α -Fe₂O₃.H₂O and γ -Fe₂O₃.H₂O) is an efficient and useful H₂S absorbant. The presence of water only improves the physical state of the purifying material and has nothing to do with the chemical

reactivity of the oxide. The simplified mechanism of reaction is given in the following equation.¹



The reaction during the revivification of the oxide may be represented as:



For revivification the presence of moisture, moderate temperature (below 50°C.) and an alkaline environment are necessary.

Experimental

(a) *The Material.*—The "Spent" Oxide containing 40 percent "S" was used in this investigation. The chemical analysis of the oxide is given in Table 1.

(b) *Activation with Sodium Hydroxide Solution.*—(i) "Spent" oxide (100 mesh) was heated in an electrically heated tube furnace in a current of oxygen until all sulphur was expelled. The studies were carried out at temperatures of 500° to 950°C. with an interval of 50°C. The residues were found as such to have negligible H₂S absorption capacity.

TABLE 1.—CHEMICAL ANALYSIS OF "SPENT" OXIDE AND CINDERS.

| Sample | Loss on ignition % | SiO ₂ % | Fe ₂ O ₃ % | Al ₂ O ₃ % | CaO % | MgO % |
|---------------------------|--------------------|--------------------|----------------------------------|----------------------------------|-------|-------|
| "Spent" oxide | 62.1 | 5.2 | 27.2 | 3.0 | 0.6 | 1.5 |
| Cinders after "S" removal | 12.33 | 12.47 | 56.0 | 15.09 | 2.01 | 2.2 |

(ii) This method is based on the reaction of ignited Fe_2O_3 with 80 percent sodium hydroxide solution.² On boiling ferric oxide and sodium hydroxide solution mixture for several hours, the former is converted to sodium ferrite which on dilution to about 40 percent strength is hydrolysed to ferric hydrate and caustic soda. For this method the cinders (residues) were obtained by burning "Spent" oxide over a Meker Burner (temperature 500-600°C.) until sulphur was expelled. The effect of time variation in boiling on the conversion of inert Fe_2O_3 to active ferric hydrate was studied. The results are presented in Fig. 1 which show that the maximum conversion occurs on boiling the mixture for 4-5 hours.

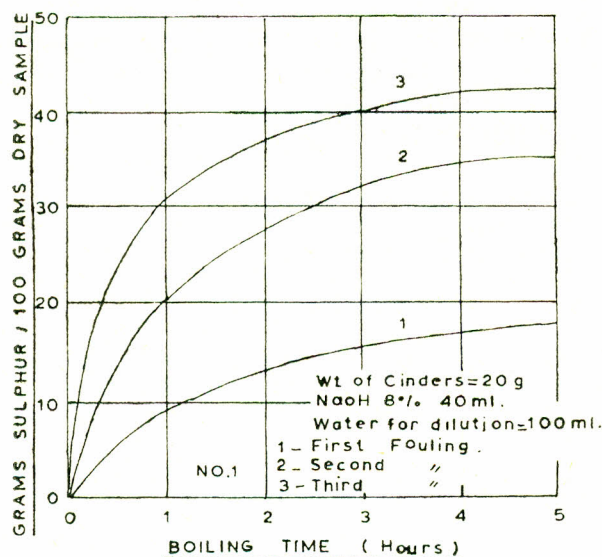


Fig. 1.—Reactivity of NaOH-activated cinders.

The activation with sodium hydroxide solutions of lower strengths were then studied by boiling cinders (20 g.) with sodium hydroxide (40 ml.) for four hours. The results are shown in Fig. 2, from which it can be seen that the activated cinders with 38 percent H_2S absorption capacity can be obtained by using 40 percent sodium hydroxide solution and thus there seems to be no need to use sodium hydroxide of higher concentration.

The pH of the activated cinders used was adjusted in the range of 8.6-9.3 by repeated washings with water. The H_2S absorption capacity was measured by the method earlier reported by the

authors.³ The flow rate of H_2S was maintained at 1.5 cm./second.

(c) *Activation with Sodium Carbonate.*—Activation of cinders with sodium carbonate solutions in concentrations of 5 percent to saturated was studied. The cinders thus activated showed low H_2S absorption capacity, the maximum of 29 percent with the saturated sodium carbonate solution.

The activation of "Spent" oxide cinders by heating with solid sodium carbonate (soda ash) was also investigated. The cinders and sodium carbonate mixtures in the ratio of 1:1, 1:1.33, 1:1.5 and 1:2 by weight were heated for one hour at temperatures 800°C., 850°C., 900°C. and 950°C., at each temperature all the four mixtures were charged. The mass on cooling was crushed and treated with water when sodium ferrite previously formed hydrolysed. The mass at 900°C. and

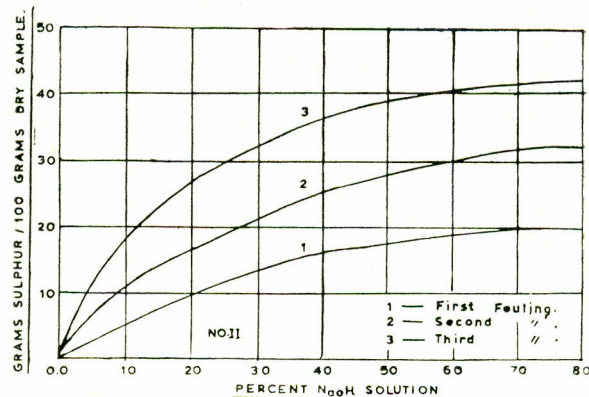


Fig. 2.—Influence of NaOH concentration on reactivation of cinders.

950°C., almost fused and the product obtained showed very low H_2S absorption capacity. The products obtained by heating at 800°C. also showed low H_2S reactivity indicating incomplete reaction between sodium carbonate and inactive Fe_2O_3 . The hydrate obtained by heating at 850°C. showed high H_2S absorption capacity. The results of H_2S absorption with the products obtained at this temperature are shown in Table 2.

From Table 2 it is evident that the reactivity as well as the total absorption capacity of the hydrate obtained from 1:1 cinder sodium carbonate ratio is optimum. It has a sulphur content of 36.70 after 3rd fouling. The results obtained with 1:1.5 mixture are very similar to those obtained by 1:1 mixture, the former has a sulphur

TABLE 2.—H₂S ABSORPTION CAPACITY OF SODIUM CARBONATE ACTIVATED CINDERS. GRAMS H₂S ABSORBED/100 g. DRY SAMPLE.

| S. No. | Cinders: Na ₂ CO ₃ ratio | Fouling | % H ₂ S absorbed after minutes | | | | % S after 3rd fouling |
|--------|------------------------------------------------|-------------|-------------------------------------------|------|------|------|-----------------------|
| | | | 15 | 30 | 60 | 90 | |
| 1. | 1:1 | 1st fouling | 22.8 | 28.4 | 32.5 | 34.8 | |
| | | 2nd fouling | 25.0 | 31.5 | 38.0 | 43.5 | |
| | | 3rd fouling | 15.0 | 23.7 | 34.0 | 38.5 | 36.70 |
| 2. | 1:1.33 | 1st fouling | 19.0 | 25.0 | 28.5 | 32.0 | |
| | | 2nd fouling | 21.5 | 27.5 | 34.0 | 41.0 | |
| | | 3rd fouling | 12.0 | 21.0 | 28.5 | 35.5 | 32.50 |
| 3. | 1:1.5 | 1st fouling | 16.4 | 25.0 | 32.5 | 36.5 | |
| | | 2nd fouling | 21.0 | 31.0 | 40.0 | 46.0 | |
| | | 3rd fouling | 15.0 | 22.5 | 31.5 | 34.0 | 37.68 |
| 4. | 1:2 | 1st fouling | 9.0 | 15.0 | 20.0 | 21.5 | |
| | | 2nd fouling | 10.5 | 14.0 | 17.0 | 18.5 | |
| | | 3rd fouling | 17.5 | 27.5 | 35.0 | 41.0 | 24.8 |

content of 37.68 percent after the third fouling. However, a gain of only 1 percent in sulphur content is out weighed by the 50 percent increase in the amount of sodium carbonate used for activation. The results with 1:1.33 mixture are comparatively lower. The hydrate obtained from 1:2 mixture shows very low H₂S absorption in the 1st and 2nd foulings. In the third fouling it shows abnormally high reactivity. This may be due to the fact that the material obtained in this case is hard, caked and less porous owing to the presence of excess alkali and hence in first two foulings it does not open up much surface area for H₂S absorption. However, on revivification after second fouling, the physical breaking up of the oxide into a freer mass takes place, resulting in greater H₂S absorption.

The H₂S absorption capacity of the sodium carbonate activated cinders was determined by Mortlake method.¹ The absorption of pure and dried H₂S was studied at intervals of 15, 30, 60, and 90 minutes.

The H₂S absorption capacity of the activated hydrate obtained from 1:1 cinder-sodium carbonate mixture was compared with that of the imported "Luxmasse" as the latter purifying material is being used in Pakistan for gas purification in the dry process. The results of the first fouling of the activated material and the original "Luxmasse" are compared in Fig. 3. The two materials show about identical reactivity.

RECOVERY OF SULPHUR FROM "SPENT" OXIDE

Pakistan has very limited resources of sulphur. According to Iqbal Ahmad and Karimullah,⁴ even at the present low rate of consumption of sulphur in the country the indigenous sulphur deposit is just sufficient to meet the demand of the country for sulphur over a period of two years. Hence the need for exploring alternative sources of free sulphur is imperative.

In European countries and U.S.A., organic solvents like CS₂, benzene, toluene and ethylene dichloride have been used for extraction of sulphur

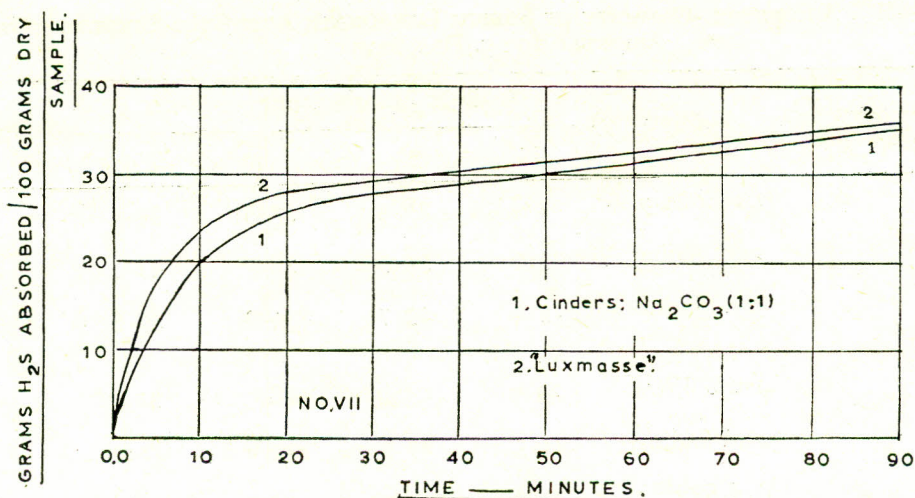


Fig. 3.—Reactivity of sodium carbonate-activated cinders and luxmasse.

from "Spent" oxide. Besides the hazards of toxicity and inflammability, the organic solvent methods usually do not yield pure sulphur. It is generally occluded with tar. In Pakistan recovery of sulphur by organic solvents is not feasible on industrial scale because of nonavailability within the country and their high cost. It was, therefore, attempted to recover sulphur from "Spent" oxide by using inorganic chemicals.

Procedure

Sulphur was recovered by treating "Spent" oxide with 5 percent (w/w) commercial sulphuric acid

which dissolved most of iron and other soluble impurities. The sulphur content in the residue increased to 66 percent. The residue after washing and drying at 105°C. was distilled in an iron retort heated over a coal fired furnace. The temperature was maintained at 500-600°C. by adjusting the air blow. The temperature was recorded by vapours of a pyrometer. Sulphur distilled over as vapours and liquid and was collected in a glass chamber cooled by water. The results of sulphur recovery are given in Table 3. Sulphur of 98.9 to 99.3 percent purity was obtained. Analysis of the recovered sulphur is shown in Table 4. The redistillation yielded sulphur of 99.8 percent purity

TABLE 3.—RECOVERY OF SULPHUR FROM "SPENT" OXIDE.

| Residue left after treatment with 5% H ₂ SO ₄ (g) | "S" Content in residue % | Recovered "S" (g) | Recovery % | Purity % |
|-------------------------------------------------------------------------|--------------------------|-------------------|------------|----------|
| 306.6 | 65.3 | 168.6 | 84.3 | 98.9 |
| 310.3 | 64.5 | 164.0 | 82.0 | |
| 304.2 | 65.8 | 160.0 | 80.0 | 99.2 |
| 303.9 | 65.8 | 198.4 | 98.2 | |
| 309.7 | 64.5 | 194.8 | 97.4 | 99.3 |
| 302.3 | 66.2 | 176.8 | 88.4 | |
| 304.5 | 65.6 | 181.6 | 90.8 | 99.2 |
| 310.2 | 64.5 | 186.0 | 93.0 | |
| 307.9 | 65.0 | 180.4 | 90.2 | 99.2 |
| 307.1 | 65.0 | 184.8 | 92.4 | |

"Spent" oxide (100 mesh) taken = 500 g. Percentage of "S" in "Spent" oxide = 40%. "S" Content in 500 g. "Spent" Oxide = 200 g.

TABLE 4.—ANALYSES OF RECOVERED REDISTILLED SULPHUR.

| S. No. | Moisture % | Ash. % | H ₂ S % | Acidity (as H ₂ SO ₄) % | Organic matter % |
|--------|------------|--------|--------------------|------------------------------------------------|------------------|
| 1. | 0.52 | 0.05 | 0.005 | 0.21 | 0.21 |
| 2. | 0.42 | 0.06 | 0.006 | 0.12 | 0.15 |
| 3. | 0.38 | 0.04 | 0.005 | 0.19 | 0.14 |
| 4. | 0.42 | 0.02 | 0.004 | 0.20 | 0.17 |
| 5. | 0.48 | 0.04 | 0.005 | 0.19 | 0.16 |

ANALYSES OF REDISTILLED SULPHUR

| | | | | | |
|----|------|------|-------|-------|------|
| 1. | 0.05 | 0.02 | 0.001 | 0.004 | 0.12 |
| 2. | 0.06 | 0.03 | 0.002 | 0.002 | 0.10 |
| 3. | 0.03 | 0.02 | 0.001 | 0.005 | 0.14 |
| 4. | 0.04 | 0.01 | 0.001 | 0.004 | 0.14 |
| 5. | 0.06 | 0.02 | 0.001 | 0.003 | 0.12 |

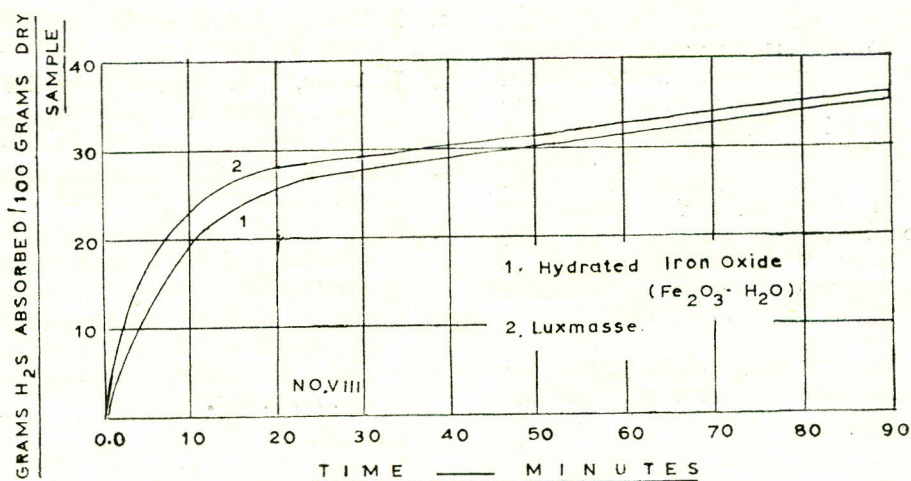


Fig. 4.—Reactivity of precipitated iron oxide and Luxmasse.

(Table 4). It is free from tar, arsenic and selenium and is suitable for use in bleaching sugar, other edible products, and wood pulp. It may also be used in rubber industry and as a fungicide.

The filtrate with 5 percent sulphuric acid is rich in Fe⁺⁺ and Fe⁺⁺⁺ iron (70%). The Fe⁺⁺ iron may be oxidized to Fe⁺⁺⁺ iron by passing air to the hot solution and then on passing ammonia into the

solution hydrated ferric oxide may be precipitated.⁵

The precipitated iron oxide shows a reactivity quite similar to the fresh "Luxmasse" (Fig. 4).

This may be recycled for gas purification even as such or in admixture with the "Luxmasse" giving better results. Almost entire quantity of

5 percent sulphuric acid (excepting minor loss in handling and working etc.) used for sulphur extraction is recovered as ammonium sulphate, which is the major product of Pak. American Fertilizer Factory. Ammonia required for this purpose is already available in plenty at the factory. With the recovery of ammonium sulphate as a by-product and formation of hydrated iron oxide of high reactivity, the method of recovering sulphur from "Spent" oxide by 5 percent sulphuric acid becomes economically feasible under the existing conditions at Pak. American Fertilizers Ltd., Iskandarabad.

Conclusions

"Spent" oxide from Pak-American Fertilizer Factory can be activated by roasting in air at 500-600°C. and treating the cinders obtained with 40 percent sodium hydroxide solution. The cinders having 38 percent H_2S absorption capacity can be obtained by this method. Sulphur dioxide produced during roasting may be recycled to the sulphuric acid manufacturing plant of the factory. The high cost of sodium hydroxide and its corrosive nature renders it unsuitable for large scale activation.

The sintering of cinders from "Spent" oxide with sodium carbonate (1:1 by weight) at 850°C. and subsequent treatment with water yielded hydrated iron oxide of H_2S absorption activity similar to that of original "Luxmasse". It has a sulphur content of 36.70 percent after third fouling. Activation by sodium carbonate seems to be economically feasible. It would enable the use of hydrated iron oxide for H_2S removal over and over again with practically no replacement of fresh oxide. The economics of this process have not been investigated.

Alternatively "Spent" oxide may be utilized for the recovery of sulphur. Sulphur of 99.8 percent

purity suitable for various indigenous industries can be obtained by treating "Spent" oxide with 5 percent sulphuric acid and distilling the residue. About 90 percent of the total sulphur present in "Spent" oxide is recoverable by this method. Hydrated ferric oxide and ammonium sulphate are obtained as by-products. The precipitated hydroxide shows high H_2S absorption capacity and could be recycled for this purpose. In ammonium sulphate almost the entire quantity of 5 percent sulphuric acid originally used is recovered. Sulphuric acid and ammonia are available at Daud Khel Factory. These factors render the recovery of sulphur economically feasible by the sulphuric acid method under the factory conditions.

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