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PRODUCTION MECHANISM OF MANGANESE SULPHATE FROM INDIGENOUS ORE

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Experimental conditions have been established for the production of industrial and agricultural grade manganese sulphate monohydrate from an indigenous manganese ore. Pulverised ore of the particle size 250 mesh, upon reaction with sulphur dioxide for 90 minutes is converted into manganese sulphate. The manganese salt free from dithionate as well as iron impurities was obtained by diluting sulphur dioxide gas with air prior to its reaction with manganese ore. A mechanism for the reaction between manganese ore and sulphur dioxide gas has been suggested.

INTRODUCTION

Manganese sulphate is an important salt for both agriculture and industry. According to a survey of the Pakistan Agricultural Research Council manganese deficiency in the Pakistan soils is acute. Various salts of manganese ore are imported from different sources for agricultural and industrial use. The main reserves of manganese ore have been reported in Lasbela [1], Kohat and Abbottabad [2] areas. However, major commercially workable deposits exist in the Lasbela district which can be exploited to produce manganese salts to substitute imports. A successsful attempt has been made in these Laboratories to produce manganese sulphate and the results are reported in this paper.

Several attempts to produce manganese sulphate from manganese ore have been made by various workers. Mayer [3], and Mayer and Schramm [4] found that manganese dioxide dissolved in an aqueous solution of sulphur dioxide formed manganese sulphate and dithionate. These processes, however, suffered from the limitation of yielding impure products. A method by Wienezy Slau [5] based on roasting, separation and leaching with sulphuric acid was reported to yield a purer product. The ore was roasted at 900-1000° and treated with 18 % sulphuric acid. On filtration, it yielded crystalline manganese sulphate ($MnSO_4$ $4H_2O$). In 1953, Blumberg and Morgan [6] converted manganese dioxide into manganese sulphate by treating manganese ore at 300-400° with a gaseous reactant containing 15 % sulphur dioxide. The above processes, however, required high temperature.

The Council of Scientific and Industrial Research, India [7] described methods based upon reducing agents other than sulphure dioxide. Manganese sulphate was obtained by digesting the crushed ore with dilute sulphuric acid in the presence of an organic reducing agent like sugar, or molasses, or sawdust, or aldehyde or various other saccharides. Ramos [8] reported the studies using propane, butane, carbon black, bagasse and sawdust as a reducing agent. The processes required several purification steps, making it less economical.

The present paper describes a simple and economical method of making pure manganese sulphate monohydrate free from impurities encountered in the above methods, utilizing local manganese ore and sulphur dioxide.

EXPERIMENTAL

Meterials

Physical characteristics of materials. All the samples from Lasbela district have more or less similar appearance. These are invariably lumpy and massive in form. The streak tests of the samples were well defined. No regular and perfect pattern of the cleavage was observed. The samples disintegrated poorly and indistinctly into pieces.

Table 1 shows the quantitative analysis of the constituents present in the Lasbela sample. Manganese, the main

Table 1. Percentage analysis of manganese ore from Lasbela District

MnO_2	Fe_2O_3	Al_2O_3	SiO_2	P_2O_5	CaO	MgO	BaO	Loss on ignition
58.0	21.2	0.5	0.20	0.12	0.5	Traces	1.2	8.2

component, was determined by the oxalate method described by Vogel [9]. Other constituents were estimated by Naseer [10] using standard analytical procedures. In order to prepare different grades of the ore, on the basis of mesh size, it was ground in a pestle mortar and the resulting powder passed through 300, 250, 150 and 50 mesh sieves. Two kg quantity of the material of each grade was collected for experimental work.

The apparatus used is shown in Fig. 1. It was specially designed to avoid the loss of sulphur dioxide gas during its reaction with the manganese ore. It consisted of funnel-shaped glass vessels with upper and lower diameters of 4" nd 1" respectively. Compressed air was introduced along with sulphur dioxide gas at the bottom. In this way thorough distribution of sulphur dioxide gas into the system was achieved and the settling of the ore was avoided.

EXPERIMENTAL PROCEDURE AND RESULTS

Removal of iron. For the removal of iron from the ore, 100 g was soaked in 100 ml of 10 % sulphuric acid for 24 hr. The supernatant was decanted and the residue washed free of the acid by successive decantation, dried and weighed. There was 25% loss in weight of ore in this process.

Preparation of manganese sulphate. The above mentioned free ore residue (95 g) was taken in the reaction vessel and mixed with sufficient water to make a litre of the slurry. A mixture of sulphur dioxide and air was introduced into the first vessel such that the unreacted gas was further passed through three vessels placed in series. 22 g of sulphur and 130 g conc. sulphuric acid were consumed to produce gas for dissolving 95 g of the ore. Samples were drawn at 15 min. intervals and analysed by the E.D.T.A. method for manganese sulphate contents [11].

The ore suspension was filtered and the residue washed with water when the formation of manganese sulphate in the ore suspension becomes constant. The filtrate and washings were heated to remove excess sulphur dioxide gas. 5 g of manganese carbonate was added to neutralise the remaining acidity. Manganese sulphate monohydrate was recovered by filtration, concentration and crystallisation of the filtrate. The yield of manganese sulphate was 75 g (75 % of the ore).

Table 2. Effect of time and mesh size on % yield of manganese sulphate

Mesh size	15 min.	30 min.	45 min.	60 min.	75 min.	90 min.
50	9%	15.35%	20.30%	25.25%	28.0%	30.2%
150	9.6%	19.2 %	31.5 %	42.0 %	48.0%	52.7%
250	13.7%	42.10%	59.5 %	69.5%	74.9%	75.0%

Effect of particle size and time. It is apparent from Figs. 2 and 3 and Table 2 that higher yields are obtained during the same reaction time from 250 mesh ore than 150 and 50 mesh ore. Therefore, it shows that the greater the surface area faster is the reaction. One can safely assume that the reaction between manganese ore and sulphur dioxide is dependant on the concentration of the ore. This fact has also been observed by Blumberg *et al.* [6] while the mesh size beyond 250 mesh has little effect on the reaction yield. It appears that the solubility of sulphur dioxide in water becomes a limiting factor at higher mesh size. Therefore, it is safe to assume that the reaction between manganese ore and sulphur dioxide gas is also dependant on the concentration of sulphur dioxide absorbed

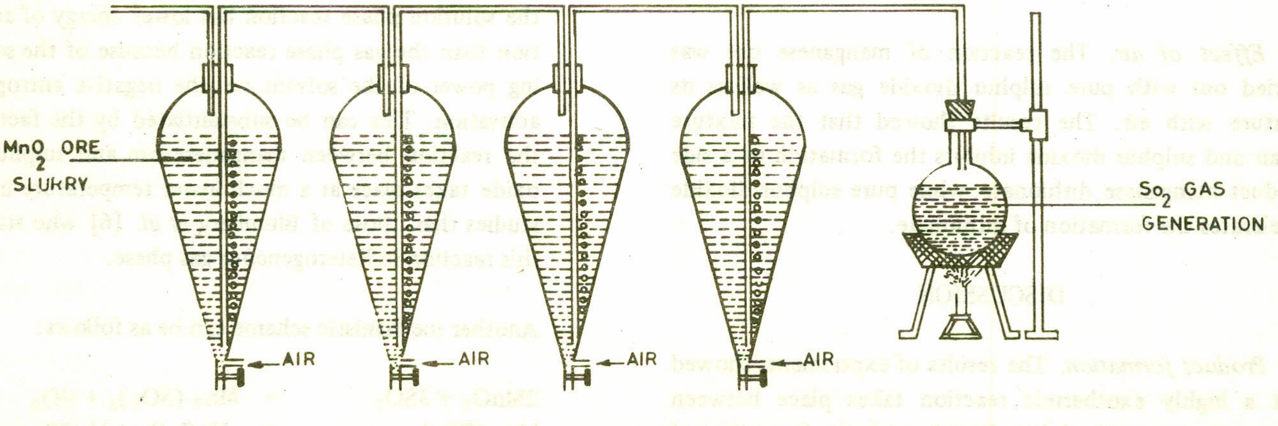

Fig. 1. Reaction vessels for the digestion of manganese ore with sulphur dioxide gas.

in the water. Blumberg *et al.* [6] also observed that reaction yields are higher at higher partial pressure of sulphur dioxide gas during the same reaction time.

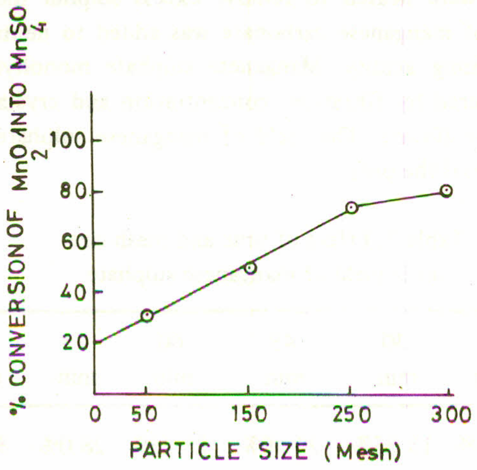

Fig. 2. Effect of particle size on the yield of manganese sulphate.

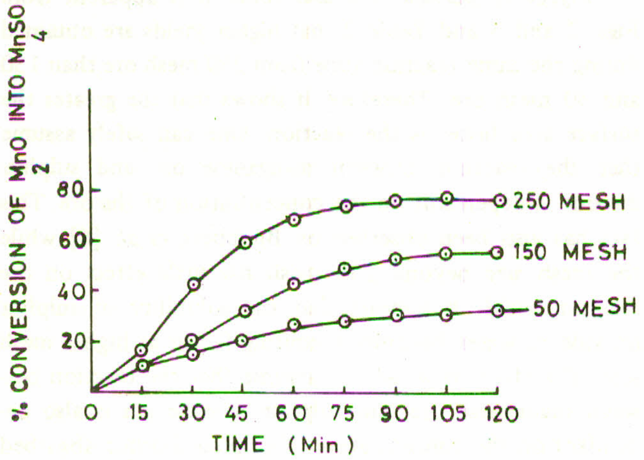

Fig. 3. Effect of time on the yield of manganese sulphate.

Effect of air. The reaction of manganese ore was carried out with pure sulphur dioxide gas as well as its mixture with air. The results showed that the mixture of air and sulphur dioxide inhibits the formation of a side product manganese dithionate, while pure sulphur dioxide accelerates the formation of dithionate.

DISCUSSION

Product formation. The results of experiments showed that a highly exothermic reaction takes place between manganese ore and sulphur dioxide with the formation of water-soluble manganese sulphate. For the experiments either pure sulphur dioxide or mixture of sulphur dioxide and air, in varying ratio, were used as feed gas, and it was found that reaction occurred when sulphur dioxide contents of the gas stream was very low. A series of experiments were conducted with different mesh size of manganese ore with gas compositions and flow rates substantially constant. The details of conditions and results have been reported in Table 2. Analysis of individual filtrates showed that manganese and sulphate ions were present in stoichciometrically equivalent amounts. Sulphur utilisation for manganese sulphate formation was, therefore, very high. Efficiency of manganese conversion based upon the analysis of filtrate and of residue were in good agreement. Therefore, information obtained on the efficiency of manganese extraction, sulphur utilisation, iron contamination, inhibition of side-product and reaction time should serve as a good basis for possible further investigation on a large scale, leading to commercial application.

Reaction mechanism. A free radical type mechanism can be discarded on the following points:-

(a) Oxygen, a free radical trap, does not inhibit the reaction.
(b) There is no induction period for the reaction, (Fig. 2).

A number of ionic mechanisms are possible for the reaction of manganese ore and sulphur dioxide. A mechanism involving prior formation of sulphurous acid, by reaction of sulphur dioxide and water, followed by the oxidation of sulphite to sulphate ions by manganese ore is not tenable because:

(a) It is difficult to explain the observed stoicheiometry.
(b) The reaction between manganese ore and sulphur dioxide also takes place with dry sulphur dioxide gas in heterogeneous gas phase. Gas phase reactions are similar to these of solution phase reactions except that the solution phase reaction has lower energy of activation than the gas phase reaction because of the solvating power of the solvent i.e. the negative entropy of activation. This can be substantiated by the fact that the reaction between manganese ore and sulphur dioxide takes place at a much lower temperature in our studies than those of Blumberg *et al.* [6] who studied this reaction in heterogeneous gas phase.

Another mechanistic scheme can be as follows:

$$2MnO_2 + 3SO_2 \rightarrow Mn_2(SO_3)_3 + \tfrac{1}{2}O_2 \quad (1)$$
$$Mn_2(SO_3)_3 \rightarrow MnS_2O_6 + MnSO_3 \quad (2)$$
$$MnSO_3 + \tfrac{1}{2}O_2 \rightarrow MnSO_4 \quad (3)$$

This scheme is tenable if one considers the dependence of the reaction rate on sulphur dioxide and manganese ore and the formation of a side product, manganese dithionate. It fails to explain the observed stoicheiometry. According to above scheme manganese sulphate and manganese dithionate should be formed in equimolar amounts, which was not observed. Furthermore, it fails to explain the addition of air in the sulphur dioxide stream which inhibits the formation of a side-product, manganese dithionate.

A competitive mechanism involving absorption of sulphur dioxide gas on to the surface of manganese dioxide ore followed by electrons transfer is preferred due to the following reasons:

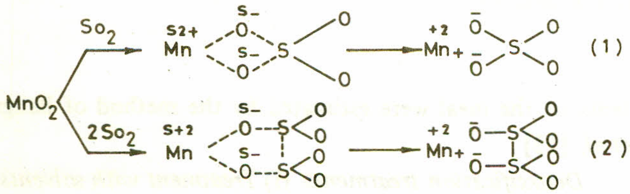

Fig. 4. Competitive mechanism of SO_2 absorption.

(a) It explains the dependence of the reaction rate on manganese ore and sulphur dioxide.

(b) It explains that reaction product should contain more of a side-product, manganese dithionate, when the concentration of sulphur dioxide is higher in the gas stream and less of a side-product when carried out with a mixture of sulphur dioxide and air in varying ratios.

(c) The reaction should proceed at lower temperature in solution phase, due to highly solvated transition state, than in heterogeneous gas phase [6].

(d) It also explains the observed stoicheiometry.

(e) This reaction mechanism requires a reaction coordinate similar to that of SN_2 reaction at the carbon centre. Reactions 1 and 2 may have same energy of activation but manganese dithionate, a minor reaction product, has certainly a higher ground state energy than manganese sulphate, a major product in the present studies. The reaction product appears to be thermodynamically rather than kinetically controlled. Thus reaction conditions leading to high sulphur dioxide concentration and low temperature should favour the formation of manganese dithionate, a thermodynamically unstable product. In fact, a standard preparation [12] of manganese dithionate requires low temperature, 0°C, and pure sulphur dioxide. These reaction conditions also produce manganese sulphate as side product. Furthermore, no manganese dithionate was detected in the reaction product by Blumberg *et al.* [6] who studied the reaction under heterogeneous gas phase at 300-400°

A conclusive evidence for this reaction mechanism can be obtained from isotope labelling experiments, which are beyond the scope of this paper.

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