Studies on Recycling of Zinc Powder in the Production of Sodium Hydrosulphite

C. AHMED BASHA, P. C. WARRIER, AL. ALAGAPPAN, K. V. VENKATESWARAN
R. VIJAYAVALLI, P. V. VASUDEVA RAO AND H. V. K. UDUPA
Central Electrochemical Research Institute, Karaikudi-623 006

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THERE are four principal methods for the production of sodium hydrosulphite, viz. chemical or zinc dust process, sodium formate method, sodium amalgam process and direct electrolytic process. Zinc powder process is the most widely adopted for the production of sodium hydrosulphite, even though the other two methods viz. the amalgam process and the sodium formate process are also well known for the purpose. The reactions involved in these methods of production are generally represented as follows :

Amalgam Process

$$2\,NaHg + 2\,SO_2 \longrightarrow Na_2S_2O_4 + 2\,Hg$$

Formate process

$$HCOONa + 2\,SO_2 + NaOH \longrightarrow Na_2S_2O_4 + H_2O + CO_2$$

Zinc process

$$Zn + 2\,SO_2 \longrightarrow ZnS_2O_4$$

$$ZnS_2O_4 + 2\,NaOH \longrightarrow Na_2S_2O_4 + Zn(OH)_2$$

In all the processes, the basic reaction is the reduction of SO_2 and the reducing agent being different in every process.

In the zinc powder process, there are two stages of reaction. In the first stage the fine zinc powder in the form of a slurry in water is allowed to react with sulphur dioxide to form soluble zinc hydrosulphite. This zinc hydrosulphite is double decomposed with alkali and zinc hydroxide is obtained as a solid by product. Sodium hydrosulphite which is in solution, is then salted out. For every ton of sodium hydrosulphite produced approximately 0.5 T of zinc powder is consumed and approximately 0.76 T of zinc hydroxide will be produced. This by-product is at present used to produce various zinc salts and zinc oxide. In an attempt to make this byproduct suitable for reuse in the same industry, a process has been developed for converting the byproduct zinc hydroxide to zinc powder. This makes the process cyclic with reference to one of the most important raw materials viz. zinc powder. This becomes more important when zinc powder for this requirement is mainly met by imports.

Direct electrochemical reduction of certain compounds of metals like zinc[1,2], lead[3,4], iron[5-7], cadmium[8-9], copper[10] and silver[11] has been studied with special reference to the preparation of the metal powders. Processes have been developed and licenced for the commercial production of the various metal powders such as zinc[12], iron[13], lead, copper and silver based on the principle of direct electrochemical reduction. As the name implies, the process involves direct electrochemical reduction of the metal compounds kept as a sediment in the solid state on a cathode metal substrate. The principle underlying the process and the various aspects of the same have been discussed in detail elsewhere[15].

The process for the production of zinc powder based on this principle has been studied with an objective of setting up a commercial prototype cell of 30000 A capacity. Based on the studies, M/s Greenland Chemicals, Vijayawada, have been licensed for production of zinc powder as an adjunct to their hydrosulphite plant. The production unit is based on a series of 3000 A cells a prototype of which has been set up and data collected from the same at the Institute.

The main objective of this paper is to present the results of the investigations of the various factors involved in the recycling of the zinc powder obtained by direct electrochemical reduction of the zinc hydroxide byproduct during the manufacture of sodium hydrosulphite. So far, the practice has been to use fresh atomised zinc powder of purity not less than 90% metallic content for each batch of production. The process of production of zinc powder directly from

the zinc hydroxide in the solid state by the direct electrochemical reduction of the same is adopted as an intermediate step and the zinc powder in the wet condition as such can be used in the hydrosulphite reactor. This obviates the necessity of using fresh zinc powder except make up for losses during handling and the process of production of hydrosulphite becomes cyclic with respect to zinc powder.

EXPERIMENTAL

The trials on recycling were carried out starting with dry zinc powder obtained from the reduction process. The zinc hydroxide obtained as a byproduct was further processed to obtain zinc powder for future trials of recycling. The process of reduction was carried out as follows : The zinc hydroxide was made into a paste and spread on the bottom of the electrolytic cell as a uniform bed. The cell served as cathode and the anode was suspended from above. The schematic diagram of the cell is shown in Fig. 1. An aqueous solution of sodium

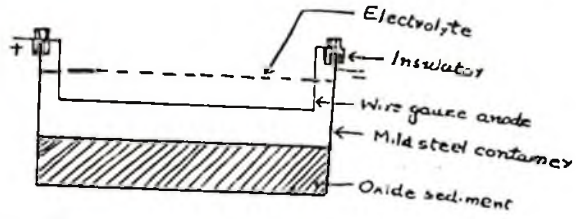
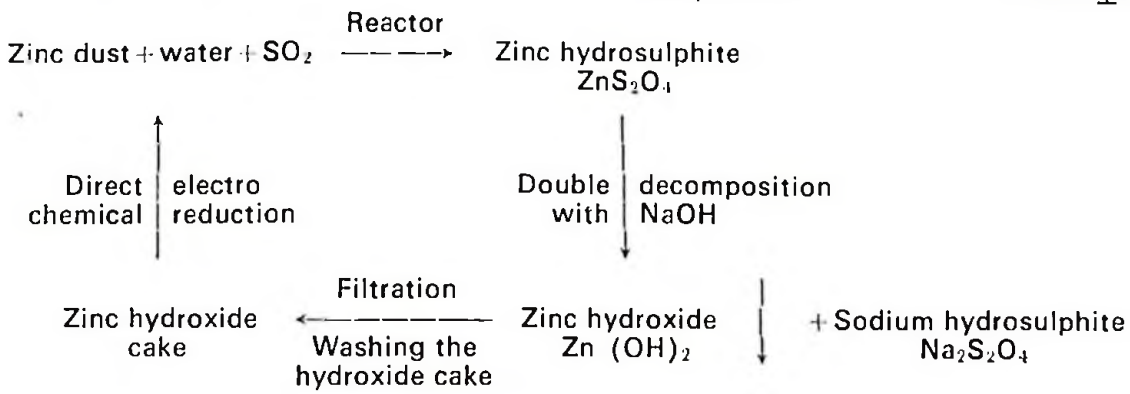


FIG. 1. SCHEMATIC DIAGRAM OF THE CELL SET UP FOR DIRECT ELECTROCHEMICAL REDUCTION

hydroxide served as the electrolyte. The flow sheet for the cycling of zinc powder is as follows :



The reactions involved in such cycling process are :

$$Zn + 2SO_2 \longrightarrow ZnS_2O_4$$
$$ZnS_2O_4 + 2\,NaOH \longrightarrow Na_2S_2O_4 + Zn(OH)_2$$
$$Zn(OH)_2 + 2e \longrightarrow Zn + 2OH^-$$
$$Zn(OH)_2 2H^+ + 2e \longrightarrow Zn + 2H_2O$$

The zinc powder obtained from the reduction cell was washed free of alkali and the wet powder was used for the subsequent hydrosulphite reactions. The experimental set up for the hydrosulphite experiments comprised a glass flask approximately 3 litre capacity with provisions for a stirrer, gas inlet and an opening for drawing samples, during the experiment. The zinc powder was suspended in water to form a slurry through which SO_2 gas was bubbled at a constant flow rate viz. 0.1g/sec Since at higher temperatures, decomposition of the hydrosulphite is enhanced, the temperature during reaction was maintained at about 30°C.

During the course of reaction, samples of solution were drawn at 15 minutes interval and the concentration of zinc hydrosulphite was estimated by iodimetry. The conversion efficiency for zinc was then calculated from the quantity of zinc hydrosulphite formed.

In order to arrive at the optimum conditions three different ratios of Zn-H_2O were tried. For this, the quantity of zinc powder was varied between 200 and 300 gms. The time for reaction was taken from the point of maximum concentration of the hydrosulphite which was also indicated by the colour of the solution. Both the hydrosulphite and sulphite were estimated during the reaction. The results are given in Table II.

On the basis of these results, the optimum conditions for the hydrosulphite reaction cycling were fixed as follows :

Slurry ratio	:	1 : 4
Mass flow rate of SO_2	:	0.1 gm/sec
Temperature	:	30°C ± 2°C

During the recycling experiments, the loss of zinc was also estimated. At every stage of the process the zinc content of the hydroxide as well as wet zinc powder were determined and the material balance for zinc was calculated. It was observed

TABLE I

Characteristics of the Zinc Powder Obtained by direct Reduction

No.	Characteristic	
	Physical	
1.	Apparent density gms/c.c	0.56
2.	Sieve analysis%	
	+ 72 mesh	2.086
	− 72 + 100	4.967
	− 100 + 200	18.58
	− 200 + 250	7.063
	− 250 + 300	11.54
	− 300 + 350	1.46
	− 350	54.29
	Chemical	
3.	Free zinc content%	92.1 − 92.3
4.	Total zinc content%	98.1 − 98.4

RESULTS AND DISCUSSIONS

Recycling of zinc powder by this method in the production of hydrosulphite introduces a new economy in the process. The cost involved in obtaining the zinc powder for the production is the processing cost and the cost of byproduct zinc hydroxide only. The efficiency of production depends largely on the characteristics of the zinc powder. Hence, it is relevant to briefly review these parameters here.

Fig. 2 shows the variation of the cell voltage and temperature during reduction of zinc hydroxide in a 500 A cell. As can be seen from the figure, the cell voltage is fairly high initially and decreases sharply to a low value which, then gradually further decreases to a steady value. On the contrary, the temperature rises with time within the first few hours and reaches a more or less steady value. It has earlier been established that the reduction of zinc oxide/hydroxide is partly by direct reduction and partly by dissolution and deposition of zinc. Dendrites or finger-like growth of zinc occurs in the early stages of reduction, which then further grow and spread in all directions within the hydroxide sediment. This results in the decrease in the IR drop across the bed and

TABLE II

Data on the Preparation of zinc Hydrosulphite from zinc Powder (Free zinc content : 90.47%)

Temp. of reaction : 31 ± 1°C Mass flow rate of SO_2 g/sec : 0.1

No.	Wt. of zinc powder taken (gms)	Ratio of Zn/H2O	Time to reach the endpoint	Concentration of ZnS_2O_4 at the end point g/l	Amount of ZnS_2O_4 gms.	Concentration of ZnSO3 g/l	Conversion efficiency %
1.	300	1 : 3	1 hr 15 mts	546.64	590.37	114.5	73.21
2.	250	1 : 4	1 hr 15 mts	503.514	604 22	64.4	82.92
3.	200	1 : 5	55 mts	441.14	507.32	78.73	94.32

that the wet zinc powder even in the unstabilised condition analysed to 96 to 98% free zinc. The results of the trials are summarised in Table III.

TABLE III

Results on Recycling of zinc Powder

1.	Analysis of zinc powder at the start :	
	Free zinc% :	90.47
	Total zinc% :	97.98
2.	Quantity of zinc powder/batch : gms :	300
3.	Number of cycles	5
4.	Analysis of the wet zinc powder (avg.) Free zinc%	96.17
5.	Duration of reaction min	60-75
6.	Concentration of zinc hydrosulphite in solution g/l	513-630
7.	Conversion efficiency for zinc powder%	90-96
8.	Loss of zinc during cycling per cycle (avg)%	10

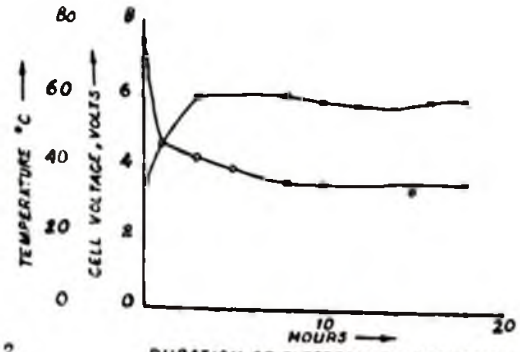


FIG. 2. VARIATION OF CELL VOLTAGE AND TEMPERATURE DURING ELECTROCHEMICAL REDUCTION OF ZINC HYDROXIDE.

there is considerable decrease in the cell voltage. After a particular stage, there is no further change in the cell voltage. Since the reaction is one partly due to dissolution and deposition of zinc, the physical characteristics of the powder are influenced by conditions of electrolysis. By proper choice of operating conditions, the reaction due to direct reduction is more predominant and thereby the characteristics of the powder are more or less constant and reproducible.

The characteristics of zinc powder obtained by direct reduction are given in Table I. The powder shows a very low apparent density; in other words, it is very light when compared to the atomised zinc powder. The rather larger particle size as seen from the sieve analysis is mostly due to agglomerates.

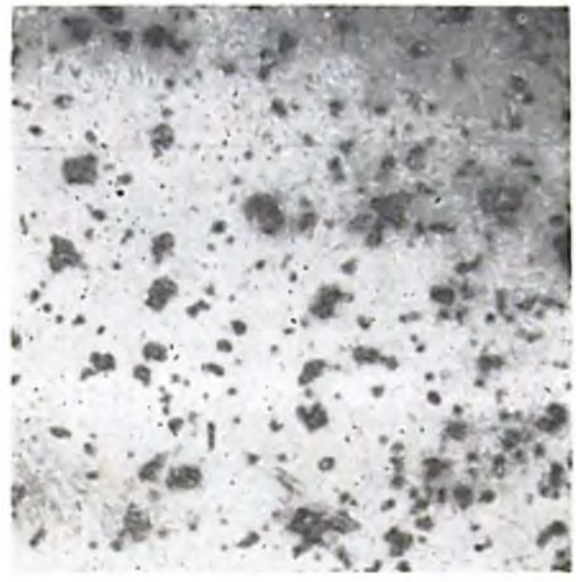
In a separate experiment, the reactivity of this powder was found out from volume and the time taken for the powder to completely react for the liberation of hydrogen. It was observed that the reduced powder was nearly twice as reactive as the atomised zinc powder for liberation of the same volume of hydrogen.

Fig. 3 shows the photomicrographs of the iatomsed zinc powder and the reduced powder. The atomised powder shows a nearly spherical shape whereas the powder obtained by direct



a

reduction is irregular in shape. Due to increased activity, irregular shape and low apparent density the chemical reaction occurs faster with this powder. Larger surface area due to irregular shape of the particles also contributes in reducing the total time for the reaction.



b

Fig. 3 Photomicrographs of (a) Atomised Zinc Powder × 100 (b) Zinc Powder by Direct Electrochemical Reduction × 150

Table II gives the data on the preparation of zinc hydrosulphite using different ratios of zinc to water. At the ratio of 1:3 the detection of end-point was not very clear and also the formation of sulphites was increased. The optimum ratio was fixed as 1:4 which was followed for further experiments.

In Fig. 4 is plotted the conversion efficiency for the zinc powder with time of reaction. It can be seen from the figure that the formation of zinc

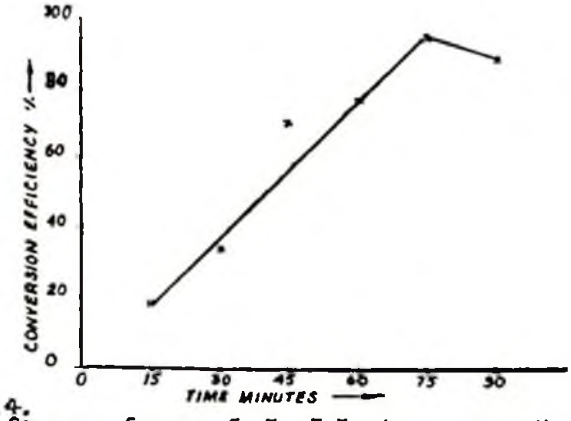


FIG. 4. CONVERSION EFFICIENCY FOR ZINC TO ZINC HYDROSULPHITE Vs TIME OF REACTION

hydrosulphite increases with time and reaches the maximum, as indicated by the peak in the curve.

On further increase, the decomposition of the hydrosulphite occurs thereby reducing the useful conversion of zinc to hydrosulphite.

TABLE IV

Trial data on the production of sodium Hydrosulphite in the Industry with Powder shown in Table III

Zinc dust taken :	50 kg
Free zinc content (when packed) :	90.47%
Total zinc content (when packed)	97.98%
Apparent density :	0.564 gm/cc
Sieve analysis :	
+ 100	8%
− 100 + 200	29.5%
− 200 + 250	8.5%
− 250 + 300	10.5%
− 300 + 350	1.5%
− 350	42.0%
Time of reaction :	1 hr. 45 min
End point detection :	Good
At the reactor after the reaction :	
Zinc hydrosulphite :	472 gpl
Sulphites :	116 gpl
At the precipitator :	
Sodium hydrosulphite :	199 gpl
Sulphites :	46 gpl

The results obtained on recycling of zinc powder in the preparation of hydrosulphite are given in Table III. Except for the starting, only wet zinc powder taken from the cell was used after washing the same thoroughly free of alkali. Loss of zinc on the average due to handling was found to be approximately 10 per cent in the bench scale. The major loss has been due to handling of zinc hydroxide and also partly during processing the zinc powder. This can be minimised while operating on a plant scale, to a considerable extent and is estimated not to exceed around 5 per cent.

The results of a trial run for testing the reduced zinc powder in the production of sodium hydrosulphite was carried out on a 50 kg zinc batch in the industry using the same powder as for the laboratory trials. The dry powder was kept on storage by the industry for over three month prior to the trial. The conditions adopted for the atomised zinc powder were adopted for this powder also. Slightly increased sulphite and a lower hydrosulphite concentration in the reactor stage indicates that slight modifications in the conditions of reaction to suit the reduced powder here to be adopted.

From the results of this study, the following conclusions are made :

1. The zinc powder obtained by direct electrochemical reduction of $ZnO/Zn(OH)_2$ is suitable for the production of hydrosulphite by the recycling process.

2. The production of sodium hydrosulphite becomes more economical by adopting the recycling process, with respect to zinc powder. Only losses due to handling will have to be made up during such cyclic use. About 95 per cent recovery of the zinc powder could be effected by the process of direct reduction and the approximate processing cost works out to Rs 3000 per tonne on a 5T per day scale..

3. The time taken for completion of reaction is less than that for the reduced powder due to high reactivity of the powder. This reduces the time per batch and hence the productivity is increased.

4. The zinc powder in the wet condition can be used directly for the hydrosulphite reaction itself and the metallic content in the wet condition is over 95 per cent. The powder in the wet condition was also found to be completely reacted.

5. High reactivity and large surface area were found to offset the low apparent density and larger aggregates.

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