THE MANUFACTURE OF SODIUM PYROSULPHITE (SODIUM METABISULPHITE)

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SUMMARY

Sodium pyrosulphite, also known as sodium metabisulphite, is useful as a convenient solid source of sulphur dioxide and, in particular, has a wide market possibility as a preservative for silage. It can be prepared by treating any basic sodium compound with sulphur dioxide. The particular case examined in the present report is based on starting with the crude sodium bicarbonate intermediate in a soda-ash manufacturing operation. Two possible manufacturing routes are explored: preparation in solution via a recycling magma of concentrated sodium pyrosulphite solution, and preparation in a semi-dry process by direct reaction with the moist bicarbonate cake.

It is concluded that the product could easily be produced at the current U.S. price of 6.6 cents/lb FOB. The primary market for local production would be as a silage preservative and since this would be a new use in western Canada, some further market studies are indicated.

INTRODUCTION

Sodium pyrosulphite, also called sodium metabisulphite, has the formula $Na_2S_2O_5$ and may be thought of as dehydrated sodium bisulphite.

$$2NaHSO_3 \longrightarrow Na_2S_2O_5 + H_2O \qquad [1]$$

It is a dry, non hygroscopic solid, highly soluble in water, under which conditions equation 1 is reversed. The sodium bisulphite is in equilibrium with a finite partial pressure of sulphur dioxide and the formation of sulphur dioxide is also promoted by acid conditions, i.e.

$$2Na_2S_2O_5 + 2H^+ \longrightarrow 2Na^+ + H_2O + 2SO_2\uparrow \qquad [2]$$

A certain amount of sulphur dioxide is also released by partial oxidation in moist air

$$Na_2S_2O_5 + \tfrac{1}{2}O_2 \longrightarrow Na_2SO_4 + SO_2\uparrow \qquad [3]$$

Sodium pyrosulphite is sometimes considered to be a solid form of sulphur dioxide since it contains 67% SO_2 (according to eq. 2). The principal use of sodium pyrosulphite is as a reducing agent and as a preservative for various food stuffs. In these applications it is being used as a convenient solid replacement for sulphur dioxide. U.S. production is about 60,000,000 lb per year and the price, which has remained remarkably stable for several years is 6 to 6.5 cents a pound at the plant.

A potential use of both sulphur dioxide and sodium pyrosulphite that has high growth possibilities for Western Canada is as a preservative for silage. In the case of grain silage (oats and barley) sulphur dioxide reduces the degree of fermentation (and hence of loss of potential food energy) that lead to acids giving natural preservation and, in the case of grass silage that is low in fermentable carbohydrates, the sulphur dioxide provides a reliable method of preservation that may be difficult to achieve naturally. Preliminary experiments by Elofson[1] with grass and by Bell[2] in Saskatchewan with oat-barley silage, have shown that the addition of sodium pyrosulphite at the rate of 10-20 lb per ton gives very striking results.

Of course, sulphur dioxide can be injected directly into the silo and Elofson[1] has shown that this may be done using suitable equipment in a pit silo. Sulphur dioxide is much cheaper than sodium pyrosulphite but the greater convenience and lower potential hazard of the latter may make it preferred for some applications.

PROCESS

The manufacture of sodium pyrosulphite is described in books on industrial chemistry[3,4] and a detailed description of the German process is given in post war reports on German industry[3]. Basically the process inovlves treating a basic sodium salt - usually sodium carbonate or sodium hydroxide - with sulphur dioxide and sodium pyrosulphite is the final product. If the reaction is carried out in solution, all components are highly soluble in water and the sodium pyrosulphite is crystallized from a saturated solution (magma) which is recycled. Commercially, concentrated solutions of sodium sulphite may also be marketed from the same manufacturing cycle. Processes have also been described for treating moist sodium carbonate with sulphur dioxide to produce the sodium pyrosulphite. The presence of some moisture is necessary for the reaction to proceed.

Manufacture from Sodium Bicarbonate

It was felt that considerable economies might be achieved if a sodium pyrosulphite facility were established in conjunction with a soda ash manufacturing plant. Furthermore, there might be savings if the feed were taken as crude sodium bicarbonate in order to save the calcining step. In a process being considered for soda ash manufacture in Alberta the crude bicarbonate is contaminated with small amounts of ammonium sulphate and sodium chloride. These should not be objectionable contaminants - particularly for a silage-grade material and should not be too difficult to remove if this were considered necessary. Consequently a preliminary investigation has been carried out of the preparation of sodium pyrosulphite from sodium bicarbonate by both a solution process and by direct reaction of a moist solid.

The reaction may be written in two steps

$$\underset{(2\times 84)}{2NaHCO_3} + \underset{(64)}{SO_2\ (gas)} \xrightarrow{\sim 50^\circ C} \underset{(126)}{Na_2SO_3} + \underset{(2\times 44)}{2CO_2\uparrow} + \underset{(18)}{H_2O} \qquad [4]$$

$$\underset{(126)}{Na_2SO_3} + \underset{(64)}{SO_2\ (gas)} \xrightarrow{\sim 50^\circ C} \underset{(190)}{Na_2S_2O_5} \qquad [5]$$

or, over-all

$$\underset{(2\times 84)}{2NaHCO_3} + \underset{(2\times 64)}{2SO_2} \xrightarrow{\sim 50^\circ C} \underset{(190)}{Na_2S_2O_5} + \underset{(2\times 44)}{2CO_2\uparrow} + \underset{(18)}{H_2O} \qquad [6]$$

In solution, the sodium bicarbonate is the least soluble of all the compounds, sodium sulphite is intermediate in solubility, and sodium pyrosulphite is the most soluble. When the reaction is carried out at 40-50°C in a saturated solution of sodium pyrosulphite the sodium bicarbonate that is charged initially may not completely dissolve. As the reaction proceeds, this precipitate may disappear and crystals of sodium sulphite appear. Then these disappear and finally sodium pyrosulphite precipitates. If moist sodium bicarbonate containing about 50% water is treated with sulphur dioxide, the intermediate stage may be a relatively mobile slurry and this then thickens up as the pyrosulphite is formed.

LABORATORY EXPERIMENTS

Laboratory experiments were carried out on both the solution and wet-cake methods. The starting material was crude wet sodium bicarbonate cake from pilot plant production by Alberta Chemicals Ltd. It was nominally 50% solids and rough analyses based on displacing the water with alcohol and ether, and also on calcining to sodium carbonate agreed on a value of 60% $NaHCO_3$, which has been used in calculation.

Solution Method

A number of preliminary preparations were made in the course of which a saturated solution (magma) of sodium pyrosulphite was built up. The following experiment describes one cycle of starting with this magma and producing a crop of pyrosulphite.

Experiment 1 - Preparation in Solution

In a 1ℓ round-bottom flask, equipped with stirrer, gas inlet and outlet tubes, was contained 550 mls of an aqueous solution saturated with sodium pyrosulphite and containing some SO_2 gas - the magma from a previous cycle. This initial solution had a density of 1.3 g/ml, a total sulphur dioxide concentration (free and combined) of 33 g/100 ml. It was assumed that 5 g/100 ml was as free sulphur dioxide and 28 g/100 ml as combined. Consequently the 550 ml initial charge contained 0.4 g moles SO_2, 2.4 g moles HSO_3^- or equivalent, and 460 g water.

Damp sodium bicarbonate (440 g, 61% $NaHCO_3$, 3.15 moles) was added slowly to avoid excessive frothing of CO_2. The addition took place over a period of 2.5 hours and the reaction mixture was slowly heated to 45° during this time. A yellowish solid was present after the addition - probably Na_2SO_3 formed by reaction of bicarbonate with bisulphite analogous to Eq. 4.

Sulphur dioxide gas was then slowly passed into the solution at about 0.35 mole/hr. The gas evolving initially was mainly CO_2. This soon ceased and SO_2 was absorbed completely. During the addition of SO_2 the solids present partially dissolved and after 8 hrs the solution had become saturated with SO_2 and a white suspension of $Na_2S_2O_5$ had formed. The total SO_2 addition was 2.8 moles. The heating was stopped and the mixture allowed to cool, during which time a very slow flow of SO_2 was maintained. At 25°-30° the solid was allowed to settle and a sample of the supernatent liquor withdrawn for SO_2 analysis (standard iodometric titration). The solid was filtered through a buchner funnel, the cake was pressed down and a limited amount of air was sucked through it. The filtrate was analysed for SO_2 and had a volume of 650 mls. The filtrate contained 33 g SO_2/100 ml as compared with 34.6 g/100 ml in the supernatent liquid. As before, the filtrate was assumed to contain 5 g/100 ml free SO_2 and 28 g/100 ml combined SO_2. Thus the filtrate contained 2.8 g moles combined SO_2 and 0.5 moles free SO_2 plus 540 g water. The cake was broken up and dried under slight vacuum at 75° in a rotary evaporator using the solution feed inlet for a hot air inlet (in other experiments hot nitrogen was used to minimize oxidation). The speed of the rotation was such that the solid tumbled rather than stuck to the sides. After 3 hr the air stream began to blow the solid about and the drying was stopped.

The yield of dried product was 235 g which contained 64.0% SO_2 and about 1.5% water (loss in weight at 100°). Taking the SO_2 on a dry basis as 65.0% gives a product purity of 96.5% assuming the impurities are substances like sodium sulphate which contain no SO_2.

The Material Balance for this experiment is as follows:

Materials In	Sulphur dioxide in solution	free	0.4 moles
		combined	2.4 moles
	Sodium bicarbonate		3.1 moles
	Water solution	460 g	
	in $NaHCO_3$	170	
	Sulphur dioxide added		2.8 moles
Materials Out	Dry product		
	combined sulphur dioxide		2.4 moles
	Filtrate		
	Sulphur dioxide - free		0.5 moles
	- combined		2.8 moles
	Water		540 g

Sulphur dioxide balance $(2.4 + 0.5 + 2.8) - (0.4 + 2.4 + 2.8)$

apparent gain 0.1 g moles

Sodium compounds (as g-ions Na^+ , assuming one Na^+ for each combined SO_2)

$(2.4 + 2.8) - (2.4 + 3.1)$

apparent loss 0.3 g ions Na^+

Water 540 - (460 + 170). Apparent loss 90 g

The balance is reasonably good, particularly in view of the rather crude assay of the wet bicarbonate charged. Some losses of sulphur dioxide would be expected but there was remarkably little evidence of free gas above the solution or form the reactor outlet so these could be expected to be small. Water will be lost during the filtering and drying step.

The increase in volume of the solution or magma over the experiment is significant. On a steady-state operation this would allow a portion of the saturated solution to be withdrawn after each cycle and further processed -- thus preventing the accumulation of impurities from the original bicarbonate. The build-up of magma in each cycle could be reduced by some degree of pre-drying of the wet bicarbonate cake.

Preparation by the Damp Method

A possible method of manufacture was assessed to be a countercurrent flow of wet sodium bicarbonate cake against a stream of sulphur dioxide gas. This contacting could take place in an auger-type reactor with the solid moving up and the gas passing downwards. Some agitation of the solid would be desirable and also the counter-current flow pattern is important for efficient sulphur dioxide recovery. Predrying of the bicarbonate cake, if necessary, and drying of the pyrosulphite product could be achieved in extensions to the reactor.

It was not considered feasible for preliminary laboratory experiments to carry out the reaction under the counter-current conditions described above. Instead, the sodium bicarbonate was treated with a large excess of sulphur dioxide and no attempt was made to obtain a material balance for sulphur dioxide. The reactions were carried out in a modified Buechi rotary evaporator. The solid was placed in a 500 ml flask of the evaporator along with a number of porcelain rollers and when the flask was rotated about an axis at some 30° to the horizontal a good mixing and tumbling action ensued. Heated nitrogen

for drying or sulphur dioxide for reaction was introduced into the flask by means of a tube down the main axis and the flask was partially immersed in a water bath for temperature control.

The important observations and results are summarized in the two experiments described below. In the first experiment the wet bicarbonate cake was used directly as received; in the second experiment it was partially dried until it had just become free-flowing. The water content at this stage was estimated at 6%.

Experiment 2 - Bicarbonate cake as received ("Wet")

4 oz. of the damp material was placed in the flask of the rotary evaporator at 60-70° and SO_2 passed in rapidly. The solid immediately began to cake together and became a paste. Bubbles of CO_2 gas were seen to froth from this paste. After about 10 minutes there was only slight frothing and the paste had become quite mobile and dirty-yellow in color. During the next 10 minutes the paste thickened and became lighter in color. Occasionally the ceramic rollers became stuck in the paste so the flask was removed quickly and the mass broken up with a spatula. After a total of 20 minutes, the SO_2 flow was replaced by a stream of hot nitrogen (100°-110°) although the bath temperature remained 60-70°. After 1 hour the flow rate of N_2 was slowed as the product began to blow out of the reactor in the gas stream. After another half hour at a slower rate the product was removed and was found to contain 61.5% SO_2.

Experiment 3 - Partially Dried Bicarbonate Cake

The original sodium bicarbonate wet cake was allowed to dry at room temperature for 2 to 3 hours in the draught of a fume cupboard. It had then become a free-flowing powder and the water content, based on loss of weight, was 6%. Thirty grams of powder was charged to the 500 ml flask of the rotary evaporator along with the ceramic rollers as before. The flask was heated to 60° while sulphur dioxide was passed in rapidly. The powder became slightly yellowish but did not otherwise change in appearance. Droplets of water were observed in the cooled nexk of the flask. Samples were taken at various times, dried for 1/2 hour at 95° (weight loss only about 1%), and then titrated for SO_2.

The results are plotted on Figure 1 which also shows the single point from the previous experiment. The sulphur dioxide assay approaches the limiting value of 67.3% at long times - of the order of 35-40 minutes. The single point from Experiment No. 2 agrees remarkably well with the curve from Experiment 3 in spite of the greatly different water content.

These results indicate that a reaction contact time of about 30 minutes in a continuous counter-current process should be adequate to produce an acceptable dry, free-flowing powdered product. Some experimentation would be necessary to establish the optimum level of predrying of the bicarbonate cake and probably a final drying stage for the product would be necessary. These experiments would need to be carried out with reference to a particular type of reactor - e.g. an auger or special design of rotating kiln.

ECONOMIC ASSESSMENT

According to Equation 6, 168 lb of sodium bicarbonate react with 128 lb sulphur dioxide to give 190 lb sodium pyrosulphite.

The Chemical Marketing Reporter lists the following prices:

sodium bicarbonate	4 cents/lb
sodium carbonate monohydrate [soda ash	4.3 cents/lb 1.8 cents/lb]
sulphur dioxide [sulphur, crude	3.7 cents/lb 1.3 cents/lb]
sodium metabisulphite	6.6 cents/lb

Soda ash is believed to be available at 3.2 cents/lb at the glass factory in Medicine Hat. Sulphur dioxide from B.C. is available at 2.5 cents/lb but with the price of sulphur in Alberta at 0.5 cents or less, on-site generation of sulphur dioxide should be possible at less than 2 cents/lb.

Taking a price of 2.5 cents/lb for crude sodium bicarbonate in wet-cake form, and of 2.0 cents/lb for sulphur dioxide, the material cost for sodium pyrosulphite (assuming ultimate complete conversion) comes out to be 3.6 cents/lb. For the relatively simple operations involved, equipment and processing costs should be low (1 to 2 cents/lb). There should therefore be a reasonable profit potential at the current FOB market price of 6.6 cents/lb [~10 cents/lb of contained SO_2]. The competitive price of sodium pyrosulphite imported into western Canada would be higher than this due to freight but it is probably necessary to keep the cost to the farmer at 10 cents/lb or lower if any appreciable market for silage preservation is to be realized.

Market

Conventional markets for sodium pyrosulphite (preservative for wines and other foodstuffs) are unlikely to be large enough to justify a plant in Alberta, although they could absorb some of the producion of such a plant. The real question is whether the economics of beef production have changed sufficiently in the last few yeaes to make silage preservation worthwhile (at a cost of about 1.00 per ton using sodium pyrosulphite). And assuming this to be the case, what fraction of the market would be obtained by sodium pyrosulphite. Formic acid is already on the market as a silage preservative but is rather expensive. Large operations could probably use liquid sulphur dioxide economically.

The use of silage is increasing rapidly in Alberta. Present production is probably close to 1 million tons/yr and some authorities expect it to level out at about 5 million tons/yr. If 1 million tons/yr were treated with 10 lb/ton of sodium pyrosulphite, the pyrosulphite requirement would be 5000 tons/yr and the gross to the manufacturer about $650,000.

These comments are only intended to provide a preliminary picture but it is hoped that someone in the chemical and agrochemical business will give further consideration to market and manufacturing possibilities for sodium pyrosulphite. A manufacturing operation tied into a soda ash facility is considered to be the most promising prospect and the only one treated in detail here but it is possible that some other low-cost source of basic sodium compounds could be considered.

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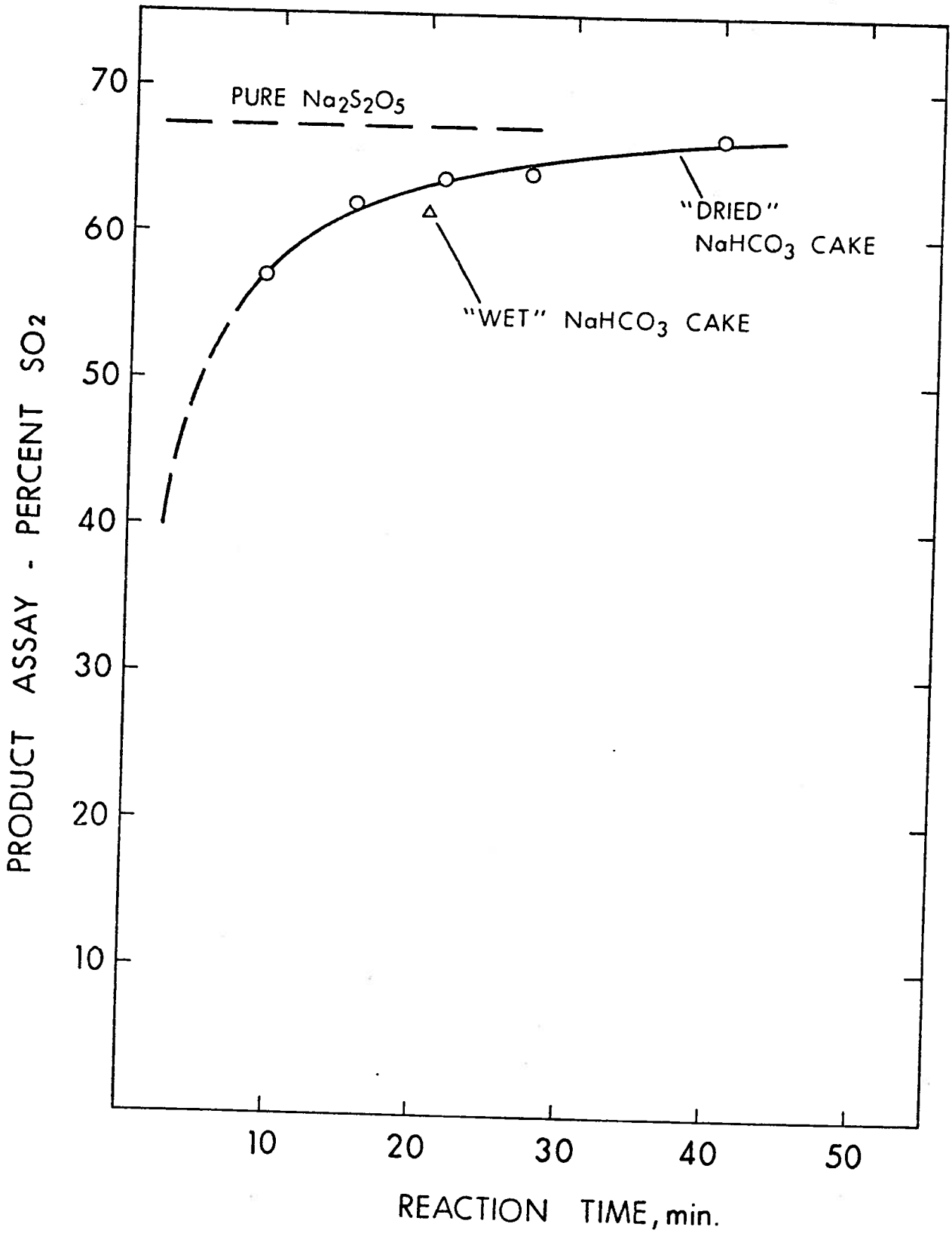

Figure 1. Conversion of damp sodium bicarbonate cake by treatment with sulphur dioxide at 60-70°C.
Data from Experiments 2 and 3.