

Deposit formation in the sulphite stage of a magnesite chemical recovery system

Ian Hamilton[^], Robert Adrien*, Daniel Baer*, Geoff Covey[~], Dennis Creasy[~], Steven Harper[#]

[^] Deceased

* Department of Chemical Engineering, The University of Melbourne

[~] Covey Consulting

[#] Kimberly Clark Australia (KCA)

ABSTRACT

A laboratory method has been developed which can reproduce the most important factors in the deposit formation in the sulphite stage of a magnesite chemical recovery system. By adjusting conditions it is possible to produce: scale-free operation, formation of free granules ('sugar'), or severe scaling. The apparatus can also be used to study or confirm the effects of adding dispersants, changing operating temperature, and changing gas composition.

It was found that the presence of magnesium sulphite hexahydrate is a sign of conditions likely to result in fouling. The causes of fouling are complex and are dependent on temperature, organics in the distillate, operating pH, sulphur dioxide concentration in the gas in the mono-sulphite section, and (possibly) inorganic impurities in the magnesia. As such, it is unlikely that a full understanding of the process can be obtained at a satisfactory cost. HOWEVER, results to date strongly indicate that some comparatively simple and inexpensive adjustments to plant operation could greatly reduce the severity of the fouling problem.

Keywords - scaling, magnesium sulphite, crystallisation

INTRODUCTION

The Tantanoola mill of Kimberly Clark Australia uses a Wagner Biro magnesite chemical recovery unit. Fouling is always a potential problem in the high pH stages of magnesite recovery. Most other recovery systems counter this by trying to minimise the formation of magnesium mono-sulphite. In contrast, the Wagner Biro system encourages the formation of the mono-sulphite to give multiple nucleation sites so that solids are encouraged to grow in the bulk of the liquid rather than on the walls

The recovery process includes a number of venturi-style scrubbers, through which the flue gas and slurry are contacted in a counter-current fashion so as to effectively remove the SO₂ from the flue gas (see Fig. 1). The bulk of the problems encountered have occurred in the final two scrubbers, units S1 and S2 and associated vessels and pipe-work. The unit S2 is the last contact stage before the flue gas is vented to the atmosphere.

Within the units S1 and S2, the addition of slurry is controlled to promote the formation of magnesium sulphite. The sulphite product produced in these two units then proceeds to further stages where the sulphite is transformed into the required bisulphite. However, at times the solid magnesium sulphite does not stay in suspension as a slurry, but crystallises on the interior walls of the units. At other times a coarse granular material ('sugar') is produced. "Scaling" is the result of crystals adhering to surfaces. Build-up of this solid formation can reach levels where the recovery process must be shut down to facilitate cleaning of the units. Such cleaning often requires physical removal of the deposits which can introduce additional risks to personnel involved in that operation (Fig 2 and 3) and results in disruption to production.



Figure 2. Build up of fouling on a vessel wall



Figure 3. Removal of deposit from a scrubber

The cause of this solid build-up on surfaces is not clear and may be due to a large number of interconnected variables. The main areas from which the problem may stem from are

the slurry introduced into the system, the recycling of condensate from the multiple effect evaporators, and the concentration of SO₂ in the flue gas. Within these two broad areas there are many variables that could each contribute to the problem. Therefore, the following objectives were set:

- (1) determine the exact nature of the solid material;
- (2) examine the effects of components in the plant condensate which could facilitate or inhibit nucleation and crystal growth;
- (3) investigate the role of some inorganic species in the magnesium hydroxide slurry, which may affect nucleation and crystal growth; and
- (4) investigate the effect of the partial pressure of SO₂ in solid formation.

REVIEW OF LITERATURE

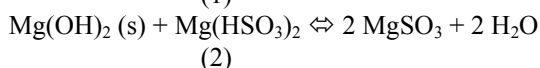
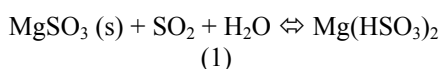
Brown and Rogers [1] described magnesium sulphite “plugging” problems in the countercurrent scrubbing of SO₂ by Mg(OH)₂ slurry at the Weyerhaeuser Timber Co’s sulphite mill, Washington (USA) wherein magnesium sulphite tended to plug the tower packing and piping when MgO was added to the last tower. The problem was overcome by increasing the proportion of magnesium oxide slurry added to the low pH (i.e. ‘early’) absorption towers.

Stevens [2] described a major problem from magnesium sulphite deposits in the scrubber unit at Fraser’s pulp mill at Edmundston (Canada). He found that the sulphite deposits were favoured by low temperature and high pH, which unfortunately were the same factors that favoured high SO₂ absorption efficiency. The trade-off at that mill was to carefully monitor pH (using a practical limit pH 6) within the temperature range used. Although Stevens gave the impression that pH control had resolved the problems at the Edmundston Mill, Cook [3] later stated that one of the causes of magnesium sulphite build up was pH-related. The sample to the pH meter was not representative and could sometimes cause excessive Mg(OH)₂ to be added to the stage, causing mono-sulphite formation. More recently, several patented processes have been published that advocate the use of dispersants in SO₂/MgO-based scrubbing systems to overcome difficulties with MgSO₃·3H₂O scaling. Jones et al. [4, 5] claimed success in the prevention of scaling using dispersing agents based on lignosulphonates. Obviously, the use of dispersants to control the problem of growth of crystalline masses in scrubber units would add to the operating costs of a mill.

In view of the vague nature of the data found in the literature it was decided that a brief experimental programme should be undertaken to examine the absorption of SO₂ by Mg(OH)₂. Initially some chemical modelling of the system would be performed using existing data. Absorption experiments would also be performed in which components of the condensate and the slurry would be investigated. The solids formed would be identified by XRD analysis and the solution would be analysed by ICP-AES.

BASIC CHEMISTRY OF THE SCRUBBER SYSTEM

Generally the formation of magnesium sulphite is believed to be an integral part of the mechanism by which SO₂ is absorbed by Mg(OH)₂. Markant et al. [6] proposed that the two important reactions involving the consumption and formation of magnesium sulphite in the production of magnesium bisulphite were:



However, in the case of the formation of deposits of MgSO₃·6H₂O and MgSO₃·3H₂O there are definitely regions in the absorptions units where SO₂ uptake does not proceed because of such factors such as pH, temperature, pressure of SO₂, solubility effects and rate effects.

EXPERIMENTAL

A carefully controlled concentration of SO₂ in N₂ was bubbled through a 500 mL reaction flask, maintained at a controlled temperature, which contained the Mg(OH)₂ slurry and any other additives being examined. An outline of the experimental rig is shown in Fig. 4.

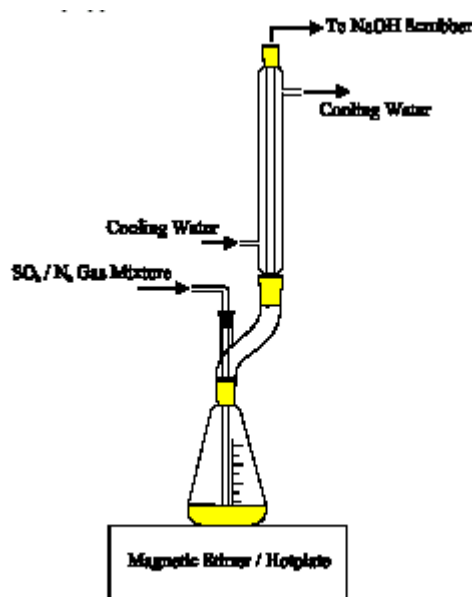


Figure 4. Experimental apparatus

It was expected that the concentration of SO₂ in the gas was likely to have a major effect on the behaviour of the slurry. Therefore, a gas mixture was generated by mixing SO₂ with an inert gas, in this case nitrogen, before introducing the gas to the Mg(OH)₂ slurry. A mass-flow meter was used which allowed the accurate metering of each gas.

Most of the analyses were conducted at the Department of Chemical Engineering of the University of Melbourne. X-ray diffraction (XRD) analyses were conducted using a PHILIPS PW 1800 instrument. X-ray fluorescence (XRF) analyses were conducted using a Siemens SRS 3000 instrument. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were conducted using a Perkin Elmer Optima 3000 instrument.

Other analyses, conducted on Kimberly Clark spent sulphite liquor condensate samples, including pH, thiosulphate (as S), sulphite, sulphate, total sulphur, and organic components were performed by Leeder Consulting, Fairfield (VIC).

In the $\text{Mg}(\text{OH})_2\text{-SO}_2$ experiments, pH was measured with an Activon model 210 pH meter using a silver/silver chloride electrode.

RESULTS AND DISCUSSION

Analysis of Solid and Liquid samples from Kimberly Clark Plant

Several solid and liquid samples were collected from the Kimberly Clark plant (Tantanoola). The solid samples included: (1) coupon samples (these samples deposited on stainless steel perforated plates immersed in the sulphite storage tank and contain both thin and thick deposits), (2) a thick white deposit (labelled S2) from inside S2's drop separator (which separates liquor from the fluegas), (3) a white solid (labelled WS1) from the absorption stage of the S1 unit, (4) a crystalline solid with white layers (labelled WS2 and WS2WL for the white layer) from the bottom of the screen tank (which screens out solids collected from cyclones in the liquor circuits around BS2, S1 and S2), (5) a "sugar" sample from the circuit around the S1 unit, and (6) various $\text{Mg}(\text{OH})_2$ slurry and MgO solid samples. Three spent sulphite liquor condensate samples were collected on different days.

The "sugar" sample from the plant was dried at 60°C and analysed by XRD. It contained only $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. When it was dried at 105°C only $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ was detected. All subsequent solid samples were dried at 60°C.

The coupon samples were shown by XRD to be mixtures of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. The difference between the thick sample and the thin sample appeared to be in the ratio of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ to $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$, the thick sample containing more $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$.

Sample S2 (8/6/00) contained $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The presence of magnesium sulphate was unexpected because of its greater solubility but its presence could be as a result of splashing and evaporation of solution in the drop separator.

The white solid (WS1) from the top of the S1 reactor contained $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ (Brucite).

The crystalline solid which also contained a white layer (WS2) contained $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. A sample of the white layer (WS2WL) was "chipped out" and was also examined by XRD which showed that it was mainly $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$.

XRF analyses of the four solids, S2, WS1, WS2 and WS2WL, showed that they contained 27-31 % MgO and 27-35 % SO_3 which would be expected for hydrates of magnesium sulphite. There were only very low levels of other elements (expressed as oxides), the only significant ones being CaO (0.14-0.36 %), Fe_2O_3 (0.08-0.10 %), MnO (0.04-0.06 %) and Al_2O_3 (0.02 %).

XRD analyses of the plant $\text{Mg}(\text{OH})_2$ sample only showed the presence of $\text{Mg}(\text{OH})_2$ whereas a sample of laboratory grade " $\text{Mg}(\text{OH})_2$ " contained $\text{Mg}(\text{OH})_2$ as well as hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). Elemental analysis by XRF did not reveal any significant differences between samples which might explain different fouling behaviour.

The furnace ash as collected is a very low-density material, reflecting its low intrinsic particle diameter and probably also indicating significant particle porosity. Because of the high specific area of the ash, it would be expected that this material would hydrate rapidly and that the resulting hydroxide would also react more quickly with SO_2 than material originating from either the laboratory magnesium oxide or plant makeup reagent. The expected behaviour is exemplified in the rapid reactions observed with plant slurries in experiments PMM11, PMM12 and PMM13 (see Table 2).

Condensate Samples

Llewellyn [7] found that the composition of spent sulphite evaporator condensate was variable and depended on factors such as the type of wood used, pH of spent liquor, inclusion of processes such as alcohol fermentation, and cooking temperatures and conditions. Apart from SO_2 , the other important components of condensate were acetic acid (0.07-8.48 g/L), furfural (0-2.92 g/L), methanol (0-1.08 g/L), ethanol (0-0.33 g/L), acetaldehyde (0-0.26 g/L) and formic acid (0.06-0.64 g/L). BOD_5 levels varied from 0.66-8.68 g/L. He stated that some researchers believed that condensate could not be used in preparation of cooking liquor whilst others showed that condensate could be used because many organic components are either consumed or destroyed under the conditions employed.

Samples (PC1, 2 and 3) of Tantanoola plant spent sulphite liquor condensate were collected on different days and were analysed for various components. The results are summarised in Table 1. Differences from the values found by Llewellyn are partly due to dilution and to segregation of

species between the various evaporator bodies. The variation in levels of impurities is such that, if one or more of them affect scaling behaviour, it would explain the observed erratic variation in plant performance.

Table 1. Analyses of Plant Condensates.

Parameter	Condensate		
	PC1	PC2	PC3
pH	1.0	1.8	2.0
Thiosulphate (as S)	63 ppm	< 53 ppm	<110 ppm
Sulphite	1300 ppm	730 ppm	810 ppm
Sulphate	1800 ppm	3600 ppm	2000 ppm
Total S	na	na	4.3 %
Formaldehyde	13 ppm	< 1 ppm	< 1 ppm
Acetaldehyde	130 ppm	< 1 ppm	< 1 ppm
Methanol	360 ppm	270 ppm	63 ppm
Ethanol	< 1 ppm	< 1 ppm	< 1 ppm
Formic Acid	1 ppm	2 ppm	< 1 ppm
Acetic Acid	180 ppm	2100 ppm	674 ppm
Furfural	33 ppm	19 ppm	1.5 ppm
p-Cymene	7.4 ppm	14 ppm	18 ppm
Eugenol	17 ppm	8.9 ppm	2.2 ppm

Scrubbing of SO₂ with Mg(OH)₂ Slurry

The analysis of plant samples indicated that the formation of various hydrates of magnesium sulphite was an important factor in the formation of the deposits in the S1 and S2 reactors. The results of a theoretical model of the system have been presented elsewhere [8]. The present paper is concerned mainly with the effects of the organic impurities.

The first series of laboratory experiments were set up to examine the effects of various organic components in the condensate.

Using the simple apparatus shown in Fig. 4, generally the volume of Mg(OH)₂ slurry was 200 mL, reaction time 8.5 hours, temperature 60°C and a mixture of 1 % v/v SO₂ in nitrogen mixture at 500mL/min was used. Most of experiments were conducted by adding only one organic component to the slurry and the composition of solid residue after reaction was determined by XRD. The results are summarised in Table 2.

In PMM1, 16% v/v SO₂ was passed through the Mg(OH)₂ slurry which reacted almost to completion in approximately 3 hours. When 1 % SO₂ was used, a reaction time of even 8.5 hrs only caused a change in pH from approximately 9 down to 7. These two experiments showed that there were more pronounced pH effects if concentrated SO₂ was used, therefore to closely follow the plant conditions 1 % SO₂ was used in most of the subsequent experiments.

Several experiments (including PMM2 and PMM3 produced highly unusual **tetrahedral** crystals (approximately 1-2 mm in length) which contained MgSO₃·6H₂O and MgSO₃·3H₂O. This unusual habit may be evidence of inhibition of growth on some crystal planes This mixture was also detected in the deposits on both the coupons. From the analysis of the “sugar” it appears that the formation of MgSO₃·6H₂O in particular should be avoided. In some of the reaction products there was crystalline material and a fine crystalline residue or in the case of PMM4 and 5 (addition of acetic acid and methanol respectively) only a fine crystalline residue formed. It is the results in which only fine crystals, or no solids at all, are formed which represent the desired outcome.

The addition of formic acid, and acetaldehyde resulted in the formation of the tetrahedral crystals. The result of methanol addition (PMM5 and 15) was quite significant because no large crystalline material formed and the fine material produced contained only MgSO₃·3H₂O, rather than the thermodynamically stable MgSO₃·6H₂O. This was a promising result. A higher concentration of methanol (PMM16) was not effective. This could suggest that if methanol could prevent sugar formation then it may only be effective in a certain concentration range.

When the plant slurry and plant condensate were reacted in the laboratory set up, the lance through which the SO₂ was introduced into the slurry started to foul. The diameter of the lance opening decreased as solid formed but it did not completely block up. In PMM12, the solid remaining after 8.5 hours was completely made up of “sugar” like crystalline material. This experiment confirms that there are also components in the plant slurry which could also contribute to “sugar” formation because there was no obvious sugar formation when the laboratory Mg(OH)₂ was reacted with the plant condensate (PMM10).

THE CRYSTALLISATION PROCESS IN THE MG(OH)₂-SO₂ SYSTEM

The system at equilibrium

The tendency of ionic species to precipitate from a particular solution can be measured by the value of the ionic product applying in that solution. In this system in question the ionic product, IP is given by:

$$IP = [Mg^{2+}] * [SO_3^{2-}]$$

Concentrations here are given in terms of moles/litre.

At pH above about 8 for the magnesium/sulfite system, the concentration of sulfite in this equation is approximately equal to the analytically determined concentration of sulfur. If the ionic product is greater than a critical limit known as the solubility product, then the growth of crystals from that solution is to be expected. Deposition of crystalline material will continue until the ionic product in the solution is equal to the solubility product for the system.

In the magnesium/sulfite system two sparingly soluble species occur: $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$. The solubility of the hexahydrate at room temperature is approximately $6 \cdot 10^{-2}$ M and the solubility of the trihydrate at 98°C is given as $4 \cdot 10^{-2}$ M. The solubility of a salt is always influenced by temperature, but these values indicate that for practical purposes in this system the solubility of magnesium sulfite is of the order of $5 \cdot 10^{-2}$ M. This figure gives a value for the solubility product of magnesium sulfite of about $2.5 \cdot 10^{-3}$. If the ionic product for a particular solution is greater than this value, crystallisation of magnesium sulfite from the solution is to be expected.

The consequences of these factors have been presented elsewhere [8] where it was shown theoretically and experimentally that while solid magnesium hydroxide is present in the system, the equilibrium solubility of magnesium sulfite is controlled by the partial pressure of SO_2 in the gas phase. This explains why earlier work on the system by another research group using pure SO_2 was unable to obtain results consistent with plant operation

Supersaturation and metastability

There can be no crystallisation of a sparingly soluble salt from solution unless the relevant ionic product is greater than the solubility product. However, it does not necessarily follow that crystals will form from solution if this condition is met. Crystallisation requires the simultaneous interaction in solution of all the species necessary to form the relevant crystal. This is an inherently improbable event and it is often the case that solutions with ionic products much greater than the solubility product behave as though they are stable. These solutions are metastable or “supersaturated” and the addition of seed crystals, or some other perturbation, is required for the process of crystallisation to commence. The slow start to crystallisation can sometimes be used to advantage to avoid unwanted effects (see e.g. [9]).

When crystallisation does commence in supersaturated solutions, the process can be extremely rapid and is often accompanied by the release of considerable heat. The difference between the ionic product for a solution and the solubility product for the system is a measure of the degree of supersaturation of the solution. It provides a measure of the driving force for the crystallisation process.

Nucleation and crystal growth

Crystallisation from a supersaturated solution proceeds by means of a two step mechanism. The first step, nucleation, is the formation of tiny crystalites from the solution. Then growth of crystals occurs on the active surfaces of these crystalites. Once nucleation has occurred, the second step tends to be very rapid and is often mass transport limited.

Nucleation is normally a slow step and it often requires a high degree of supersaturation of the solution before nucleation can commence. Nucleation is facilitated by the

presence of active surfaces in the system. Adsorption of ions from a solution onto a surface increases the concentration of the ions on the surface to an enormous extent compared with their concentration in solution. This increase in local concentration increases the probability of formation of crystalites and nucleation commences.

In the plant, the passivating oxide layer on stainless steel construction materials, insoluble ionic species in the slurry and adventitious “dirt” all provide potentially active surfaces on which nucleation may be initiated. Surfaces with similar atomic structures to that of the crystals deposited from a solution are the most effective in catalysing nucleation. The most active surfaces are usually those of remnant crystals of insoluble product left over from previous events. These are the so-called seed crystals. At Tantanoola, seed surfaces are usually provided by recirculation of slurry around each scrubber.

In solutions with very high degrees of supersaturation, the processes of nucleation and crystal growth can proceed simultaneously.

Control of crystallisation in supersaturated solutions

Very highly supersaturated solutions can be prepared from high purity reagents in scrupulously clean apparatus using high purity water filtered through very fine membranes. Such conditions do not arise in a plant situation and the presence of metastable supersaturated solutions in a plant it is usually the result of crystallisation inhibitors.

These inhibitors are usually surfactants or polyelectrolytes. They stabilise solutions against crystallisation by adsorption onto surfaces, competing for surface sites with the ionic clusters that precede nucleation of crystalites. They also adsorb on actively growing faces on pre-existing crystalites, preventing access of ions from the solution to these faces and thereby slowing crystal growth. Very low concentrations can be effective because mono-molecular coatings on growth faces can be effective in preventing growth at these sites.

In the system studied the maximum ionic product reached values of $4.0 \cdot 10^{-2}$ using distilled water and $6.2 \cdot 10^{-2}$ using plant condensate compared to the solubility product of the system of $2.5 \cdot 10^{-3}$ [8]. These values are a very strong indication that the solutions had reached a high level of supersaturation. The existence of supersaturated solutions in a normal plant environment is an indication of the presence of inhibitors in the system, whether or not they have been added consciously. The organics in process condensates (e.g. methanol and acetic acid) have the potential to act as inhibitors for the crystallisation of magnesium sulfites in the Tantanoola plant. Once scale has formed in a plant, there will be an increasing tendency for faster scale formation as it is almost impossible to eradicate all seed crystals left on a surface from an earlier scaling incident.

It is worth noting that inorganic impurities can also potentially inhibit crystallisation but preliminary experiments (not presented here for reasons of space) suggested that inorganic impurities are not significant in the crystallisation process.

CONCLUSIONS

The laboratory program has demonstrated the ability, under controlled conditions, to mimic the various forms of magnesium sulfite scaling behaviour observed in the plant. It has provided a method to prepare plant slurry for realistic laboratory measurements of supersaturation and crystallisation behaviour, including inhibition of crystallisation.

The techniques described here could be used to investigate the use of controlled addition of magnesium sulfite seed crystals to manage the habit of crystal growth from supersaturated solutions so that it occurs preferentially on slurry particles rather than on the stainless steel surfaces thus causing scaling.

The monitoring methods described here, for degree of supersaturation and inhibition status, can be applied routinely at the plant as part of quality control procedures to maintain reliable operation in the face of variations in feed and other factors.

The presence of magnesium sulphite hexa-hydrate is a danger sign. A simple weight loss on drying test on slurry solids can give advance warning of potential fouling problems.

Some organics in the condensate, particularly acetic acid and methanol help alleviate fouling problems, and preferential use of distillate from appropriate evaporator effects could be used to help control fouling.

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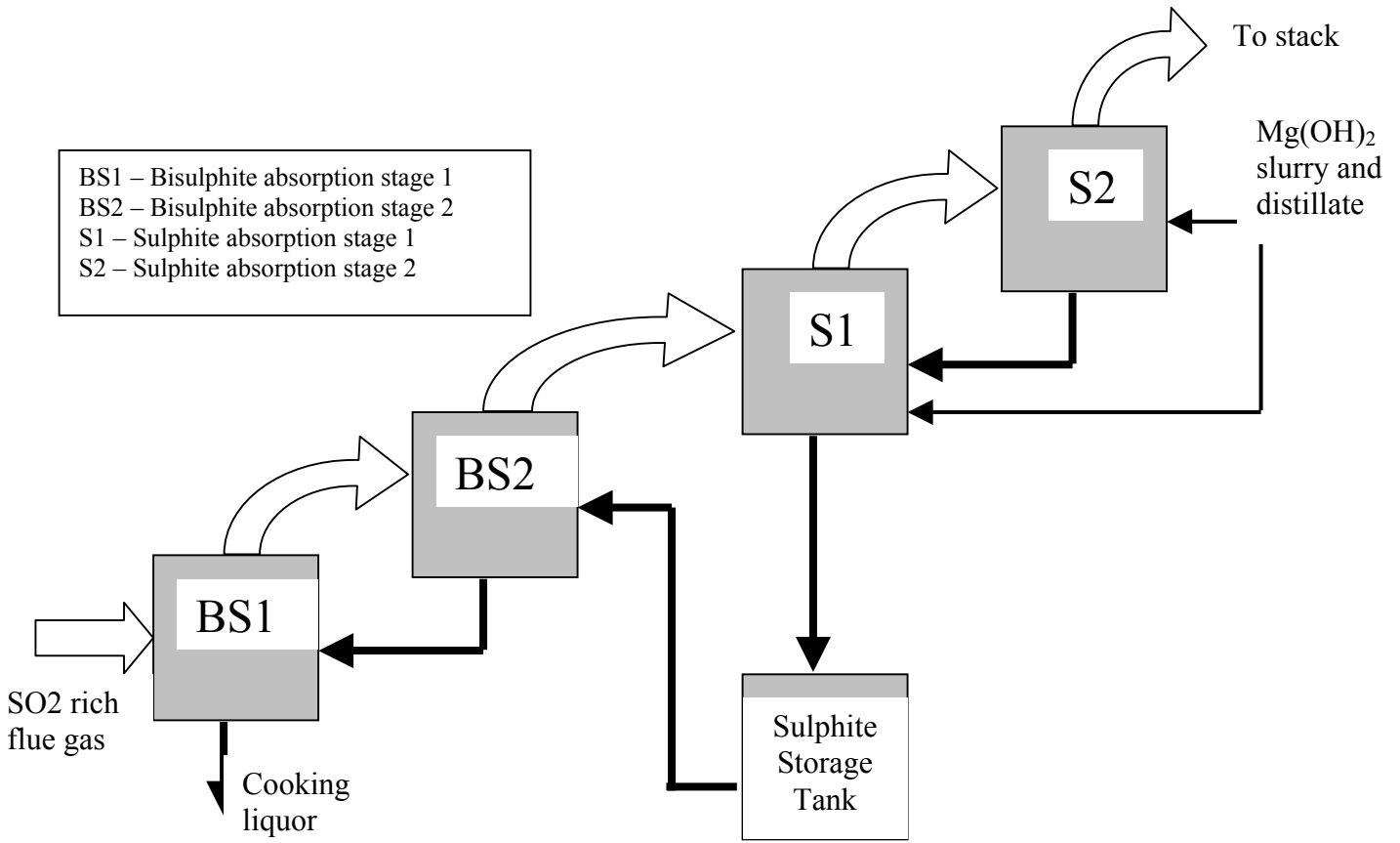


Figure 1. Schematic of the sulphur dioxide absorption train

Table 2. Summary of Absorption of SO₂ with Mg(OH)₂ Slurry Experiments-

PMM1	PMM2	PMM3	PMM4
16 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂
20g Mg(OH) ₂ / 200 mL	10g Mg(OH) ₂ / 200 mL	7.2g Mg(OH) ₂ / 200 mL	7.2 g Mg(OH) ₂ /200 mL + 10g/L acetic acid
3 hrs	8.5 hrs	8.5 hrs	8.5 hrs
Initial pH 9	Initial pH 9	Initial pH 9	Initial pH 9
Final pH 3-3.5	Final pH ~ 7	Final pH ~ 7	Final pH ~ 7
Milky slurry turns yellow	Milky slurry turns yellow	After 4 hrs. get colour change	no colour change
crystalline material gradually forms	Tetrahedral crystals form after cooling	Tetrahedral crystals form after cooling	Fine crystals at end of expt. with yellow tinge
MgSO ₃ .6H ₂ O detected	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O detected	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O detected	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O

PMM5	PMM6	PMM8	PMM9
1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂
7.2g Mg(OH) ₂ / 200 mL + 3 g/L methanol	7.2g Mg(OH) ₂ / 200 mL + 0.7 g/L formic acid	7.2g Mg(OH) ₂ / 200 mL + 0.3 g/L acetaldehyde	7.2 g Mg(OH) ₂ /200 mL + 2g/L furfural
8.5 hrs	8.5 hrs	8.5 hrs	8.5 hrs
Initial pH 9	Initial pH 9	Initial pH 9	Initial pH 9
Final pH ~ 7	Final pH ~ 7	Final pH ~ 7	Final pH ~ 7
formation. of fine crystalline material	Tetrahedral crystals form after cooling	Tetrahedral crystals form after cooling	Tetrahedral crystals form after cooling
	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O in residue	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O in residue	Scrubber solution turns yellow
MgSO ₃ .3H ₂ O detected	MgSO ₃ .3H ₂ O	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O s	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O

PMM10	PMM11	PMM12	PMM13
1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂
7.2 g Mg(OH) ₂ + Plant Condensate	Plant Slurry + Plant Condensate	Plant Slurry + Plant Condensate	Plant Condensate + Mg(OH) ₂ (9.76 g)
8.5 hrs	8.5 hrs	8.5 hrs	8.5 hrs
Initial pH 8	Initial pH 8	Initial pH 8	
Final pH ~ 7	Final pH ~ 7	Final pH ~ 7	
Tetrahedral crystals form after cooling	lance blocks up	lance blocks up	lance blocks up
Scrubber solution turns yellow		“Sugar” formation	no “sugar”
MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O	MgSO ₃ .6H ₂ O and MgSO ₃ .3H ₂ O

PMM14	PMM15	PMM16
1 % v/v SO ₂	1 % v/v SO ₂	1 % v/v SO ₂
Plant Slurry, 84mL Slurry + 116mL H ₂ O	7.31g Mg(OH) ₂ , 84mL Distilled H ₂ O + 116mL of Methanol mixture (0.75g MeOH in 250mL)	116mL Plant Distillate 84mL Plant Slurry + 2g Methanol
8.5hrs	8.5hrs	8.5hrs
Small amount of “Sugar”-like crystals, remainder very fine	Few tetrahedral crystals, remainder very fine	“Sugar”-like crystals form

