FGD Forced Oxidation Mechanism A Pilot Plant Case Study

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ABSTRACT

This is an accounting of an unsuccessful attempt to scale up an EIMCO Oxidizer design to induce air into a sulfite slurry without the use of compressed air blowers. The 300-HP prototype oxidizer was brought on-line in 2002 at the WKE Reid/Green station to oxidize a controlled feed of calcium sulfites from the plant thickener underflow.

The paper relates how the production of high quality gypsum was readily achieved and processed on site. It also presents the conclusion from numerous trials using batch and continuous modes of operation. The paper discusses unsuccessful attempts to increase the unit oxidation rate to an acceptable level. Critical design shortcomings are discussed, and a general discussion of issues affecting cost is also included. The author relates what effect the design changes had on the oxidation rate and how the knowledge was used to develop a successful oxidizer design in 2003.

The discussion also details the key considerations of feed slurry conditioning and how they relate to the overall process control. Some attention is given to the parameters for controlling the oxidation process and how they are affected by the ever varying feed chemistry. Additional information is included on how an alternative feed source was developed to eliminate the use of sulfuric acid for pH control, a major cost roadblock.

BACKGROUND

- Cost - The Cost of installing and operating a conventional sparger oxidation bubble tower is the primary driving force behind the development of new turbine oxidizer systems. FGD gypsum synthesis from scrubber-derived sulfites is a well developed technology, which is widely practiced and generally understood. The inefficiency and capital cost of installation for large sparger towers is also painfully well understood by the power industry. The conventional sparger oxidation design normally requires over 200% excess air to achieve the oxygen mass transfer required for complete oxidation of scrubber sulfites. The size of external oxidation towers can be up to 60' in height. Internal reactor retrofits can cause long term loss of generating capacity in addition to the first cost of installing the sparger system.

The use of mechanical agitation for froth flotation and waste oxidation is also a widely applied technology and would seem to lend itself readily to the oxidation of FGD scrubber sulfites. Turbine oxidizers could be sited remotely and would greatly reduce the disruption of a conventional reactor retrofit. The cost of compressed air for the conventional bubble tower oxidizer is also a major consideration. The compressor power requirement varies directly with the air pressure requirement. Bubble towers require high pressures to overcome the hydraulic head, and sparger nozzle resistance.

- Environmental - Long-term land disposal of scrubber sulfites has become increasingly indefensible as a viable alternative. The considerable cost of permitting, developing and maintaining large areas of land continues to escalate. Wet-fill land disposal has become a less attractive option as the demand for FGD gypsum continues to increase.

- Experience - In 2000 EIMCO Process Equipment applied their knowledge of froth flotation to the development of a new device to oxidize sulfites to sulfates. Originally known as the WEMCO Oxallizer sulfite oxidizer, the design was based on the well-known WEMCO Smart Cell and WEMCO 1+1 flotation machines, which were widely distributed in various mineral concentration operations. EIMCO described the application in some detail in a 2001 paper by Hayward B. Oblad, <u>Gypsum Production in a WEMCO Oxallizer Sulfite Oxidizer.</u> The machines are characterized by a centrally located Rushton-type rotor that is suspended just below the surface of the slurry.

  The theoretical capacity of the new EIMCO Oxallizer was determined by EIMCO in advance of the trial by a series of bench-top and small scale tests. The tests were conducted on scrubber slurries from six sites, including the Western Kentucky Energy Plant at Robards Kentucky, which became the site of the pilot plant installation.

EQUIPMENT

- Construction - The EIMCO oxidation vessel is a cylindrical vertical tank, which is fully rubber lined. The top features segmented covers, which are supported off the drive support structural steel. Open beams cross the top of the tank, and are supported by the tank walls. The drive support structure is above the top tank covers which are also rubber lined. The drive consists of a 300 HP motor, with belt reduction connection to a Flender right-angle speed reducer. The drive outputs 100 RPM to produce an 8 M/sec tip speed on a 60” diameter rotor. The tank working volume is 22,000 gallon.

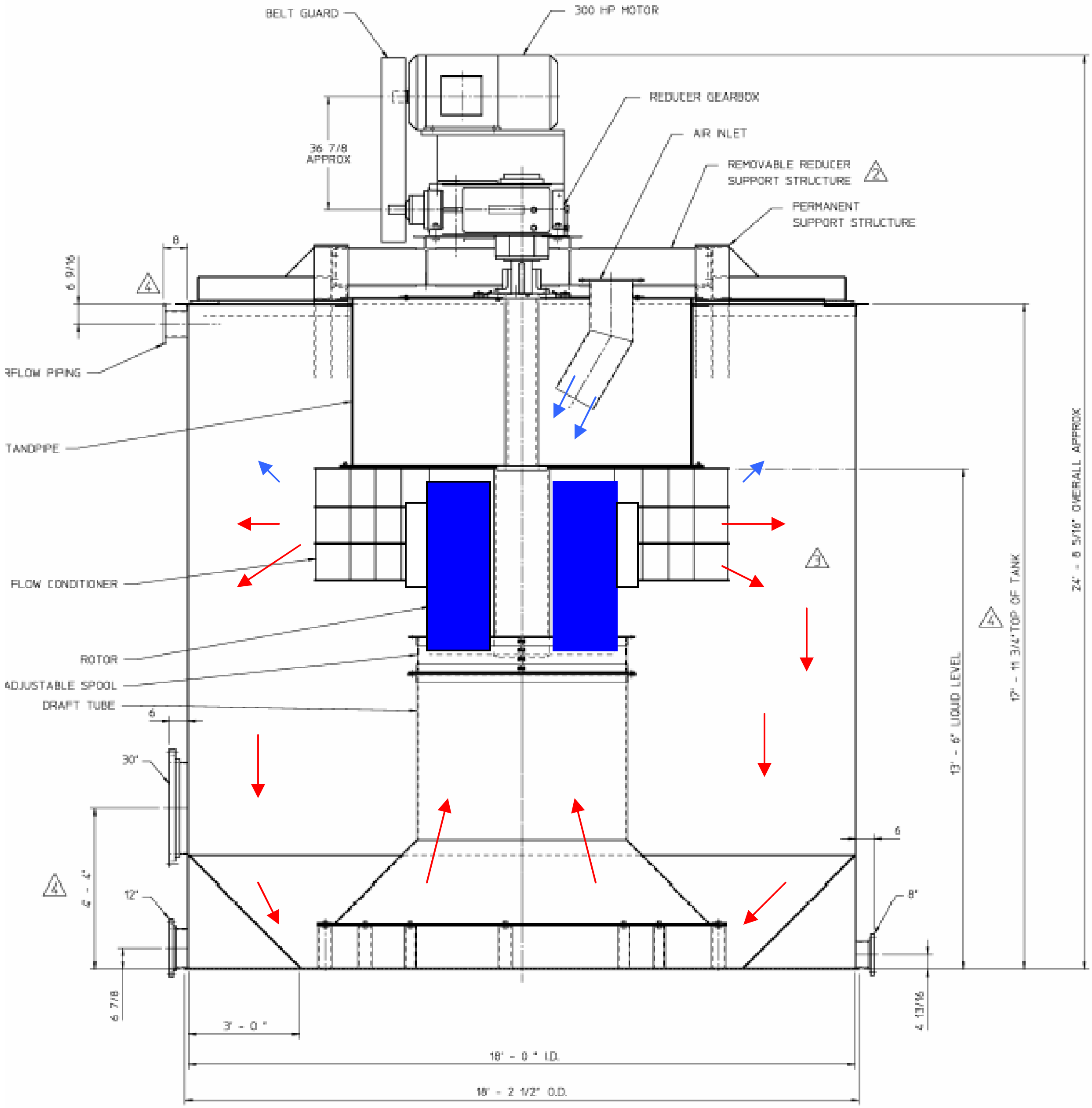


Figure 1 - EIMCO Oxidation Vessel with 300 HP Drive

Air entered the top of the vessel through a 14" ϕ duct and was drawn into the vortex of the 60"ϕ turbine below. Slurry was drawn up through the inner draft tube into the rotor and ejected outward through the cylindrical open grid. The purpose of the grid is to reduce swirl and facilitate vertical flow to re-circulate the slurry. The design is subject to high abrasion, scaling and the corrosive effects of the various reactants.

The gypsum formed by the oxidation reaction continued to grow in crystal size until it stratified near the vessel floor. All gypsum production exited the vessel through pipe penetrations near the floor. There was no air injected into the bottom of the vessel and no sparger plumbing.

- Pipes - The Thickener Underflow (TUF) slurry entered the oxidizer through the top, where it was diluted with process water inside the vessel. Both the TUF slurry and process water flows were monitored and controlled to preset values. The concentration of the TUF slurry was continuously monitored and reported to the controller. The slurry was provided from the existing thickener underflow pump. Variations in slurry feed concentration required manual recalculation and reset of the feed rates. A rubber membrane pinch valve was used to regulate the slurry flow. Pneumatic actuators controlled the valve position and regulated the slurry flow. Process water flow was controlled by a pneumatically actuated butterfly valve. Acid addition to the slurry was also through the top of the oxidizer vessel. The slurry, process water and acid are fed in the same general area for ready mixing.

- Pumps - Gypsum discharge slurry was pumped from the oxidizer using a centrifugal slurry pump with a VFD drive. All slurry piping is high density polyethylene or stainless steel, and water piping is carbon steel. The acid lines are also welded carbon steel. The process water supply was also supplied from a branch line off of an existing centrifugal pump.

  A dedicated acid feed pump was installed to provide sulfuric acid to the oxidizer. The acid feed system was controlled manually based on readings from a pH sensor in the oxidizer. Two 250-gallon acid totes were maintained at the site for an uninterrupted supply of sulfuric acid. Magnetic flowmeters were used to monitor the slurry and process water feed rates.

- Control - All sensors, valves, flowmeters and pumps reported to a central computer, which continuously displayed and recorded the critical events, motor amperages, operating levels, pH, temperature and flow rates. The TUF slurry density was measured by an existing WKE densitometer and reported to the Synmat PC for interpretation. The operation was controlled manually and with some limited automation through a single PC based HMI interface. The PC logged time, amperage, flow, pH, tank level and temperature. All equipment could also be operated manually from the MCC.

- Filtration – A 12 inch wide EIMCO horizontal belt filter (HBF) was located onsite for a one month trial to verify the handling and filtration characteristics of the FGD gypsum produced by the oxidizer. The HBF was under-sized for the oxidizer output, even though it production was less than 4 tph of gypsum at the time of the trial. A hydrocyclone was installed ahead of the HBF to concentrate the feed. The hydrocyclone was fed directly from the oxidizer discharge pump. The FGD gypsum was of a high quality and easily filtered. A 30' x 24" wide stacking conveyor was also placed on site during this phase to service the HBF. Over 200 ton of gypsum was produce over several days and stacked on site. A photo of the set up is provided below.

Figure 2 – Oxidizer Vessel in Operation with Filtration

- Laboratory - Laboratory equipment was maintained on-site for the duration of the trials. Titration of sulfites was the method chosen for determining the oxidation rate. Basic calibrated glassware, scales, and chemicals were all used continually during the trial to perform manual analysis of the oxidizer slurry. The absence of sulfites was the criterion by which the oxidation was determined to be complete. A Computrac moisture analyzer was used to determine the purity of the gypsum following completion of the oxidation. Marcy scales, portable flowmeters, sieve screens, anemometers, portable pH probes and temperature sensors were all used regularly during the course of the trial.

THEORY OF OPERATION

- Cavitation - Dr. Oblad referenced several contributors to the EIMCO theory of cavity ventilation, which was the primary mechanism by which the oxidizer was to introduce oxygen into the slurry. The cavitation occurs along the trailing edge of the rotor. For this reason tip speed and power input were considered to be closely related to the efficiency of the oxygen mass transfer. Air from above the rotor moves down and out along the back of the vanes, penetrates the cavities or voids, and stabilizes them into bubbles. The vapor pressure, hydraulic head and atmospheric pressure all affect the rate at which the air is driven into the oxidation reactor. The extreme turbulence at the rotor tip is the interface for the bubble creation. While similar to the WEMCO flotation machines, the oxidizer formed no froth and there is no launderer in the design. The bubbles are created near the surface of the slurry. The rotor must drive air into the cavities that form along the tip and then create enough flow to pull the air down with the slurry circulation.

- Flow – The concentration of the slurry was lowered to less than 20% solids by mixing the TUF slurry with process water. This is necessary to allow oxidation to begin. Mixing, oxidation, solids dissolution, and settling all occur in the oxidizer vessel simultaneously. All the solids must be dissolved before they can react, so acid, slurry, process water and air are violently blended to mechanically speed the oxidation process.

  Heavier gypsum crystals form and stratify near the bottom of the oxidizer vessel for removal through the discharge piping. The rotor also serves as a most effective pump. It rapidly moves the liquid up through the draft tube and out into the flow conditioner. The velocity of the flow can easily re-suspend solids which typically settle during system downtime. The flow also scrubbed the inside of the vessel with solids preventing the formation of gypsum scale deposits in the wetted areas.

- Oxygen Mass Transfer – Though extensively studied, oxygen mass transfer remain a complex and difficult phenomenon to influence economically. Bubble size, surface tension, pressure and agitation all affect the critical absorption of oxygen into solution. Cavitation is one way of producing small bubbles, provided they can be filled with air and diffused through the slurry.

  The EIMCO Oxallizer originally featured only a 14” ϕ air duct inlet to the vortex formed by the turbine action. A radial booster fan was attached to the air inlet near the end of the trials to increase the air supply and pressure. A similar 14” exhaust duct was eliminated in favor of a 30” diameter stack. The larger stack better accommodated the large volume of water vapor which was produced by the exothermic reaction and reduced back-pressure against the air flow.

- Modes of Operation – The oxidation process always began with a batch and could be evaluated upon complete oxidation of the batch, or allowed to proceed into a continuous mode. The controls allow for both modes of operation. The continuous mode represents normal commercial operation of the oxidizer. In order to prove the effectiveness of the oxidizer it had to eventually be brought into continuous operation. The batch mode is simply the agitation and oxidizing of a batch without additional feed or discharge until the oxidation reaction goes to completion.

- Feed Variations – The scrubber reaction continuously varies in the quantity of sulfur removed from the emissions, primarily because of varying load conditions. For this reason it was initially thought that thickener underflow would be a good source of a relatively consistent slurry feed to the oxidizer. The density of the thickener underflow varies very little, and it can be diluted easily to the desired concentration. Unfortunately thickener chemistry at WKE's Reid Green power plant contained unreacted lime. This required large amounts of acid to create optimum pH for oxidation. Later trials using feed from the absorber tower provided a slurry source which required little acid for complete oxidation. However, the concentration of the sulfites from the absorber tower also varied greatly compared to the relatively steady concentration of the thickener underflow slurry.

PROCEDURE AND THEORY

- Oxidation Rate Calculations – The bottom line calculation for this oxidation equipment is the oxidation rate and unit cost of production. Unit cost data is not included in the scope of this report. Proceeding from the basic stoichiometry, our task was to determine the tonnage of gypsum to be produced from the total calcium sulfite feed slurry. The basic reaction is described by the following equations:

<u>Oxidation</u>:

$2\ HSO_3^- + O_{2(g)} \rightarrow 2\ SO_4^{-2} + 2\ H^+$ Note liberation of hydrogen ion.

$2\ SO_3^{-2} + O_{2(g)} \rightarrow 2\ SO_4^{-2}$ Would only occur at low pH.

Forced oxidation of calcium sulfite in FGD slurry to form gypsum requires both oxygen and calcium sulfite to be dissolved. The actual reaction between dissolved oxygen and dissolved sulfite (or bisulfite) is rapid. The observed rate depends on the rates of these two materials dissolving, and may be limited by a variety of factors.

<u>Gypsum Formation</u>:

$Ca^{+2} + SO_4^{-2} + 2\ H_2O \rightarrow CaSO_4 \cdot 2\ H_2O_{(s)}$

The actual calculation becomes complicated in the continuous mode, as flow rate, tank level and slurry concentration changes continuously. Electronic data collection allowed us to accurately measure the changes and compute average values for relatively short trial periods. A sample trial report is shown below for reference only.

Description of trial:	**6700 GPH Absorber Slurry**		
Date:	**10/10/02**	Feed % solids	8.8

Part I: Data

	C	D	E	F	
Information:	Start	End	Average	Change	Units
Test Period:	2:15	4:00		1.75	hours
Tank pH	5.32	5.05	4.96		
Water Feed Rate			0		gal/hr
Slurry Feed Rate	6705	6638	6724		gal/hr
Slurry % Solids	10.30	7.35	8.830		%
Tank Level	13.58	13.69	13.60		ft
Tank Sulfite g/L Titration	0.64	0.90	0.592		g/L
Acid Feed Rate			8.3		gal/hr
Discharge Solids %			14.6		%
Slurry Sulfite g/L Titration	79.34	73.5	76.5		g/L
Slurry Density	1.08	1.06	1.072		g/mL
Tank Volume	19160	19370	19200		gal
Temperature	140	153	146		

Part II: Reaction Rate Calculation

	TPH with cumulative corrections	Effect of this correction	
Feed: Total Solids	**2.651**		
Corrections made for:			
Actual sulfite in feed	2.142	Multiplied by	0.8082
Sulfite in discharge		Subtract	0.0166
Change in tank contents		Subtract	0.0123
Net Oxidation Rate	**2.114**		
TPH Gypsum Produced:			
From oxidation:	2.818		
From hemi-hydrate sulfate in feed:	0.533		
From acid conversion of carbonate in feed:	0.036		
From acid conversion of lime (fast) in feed:	0.007		
Total Gypsum TPH	**3.394**		

Figure 3 - Typical Trial Result Report

- Parameters – During the course of all the trials, various parameters were controlled to measure their influence on the oxidation rate. These included the pH, tank slurry level, slurry concentration, and chemistry. Other system changes were made to the air supply, rotor speed and feed source, but these were not controlled or varied by the operator during the course of a trial. The effects of each variation were measured for the oxidation rate and gypsum purity. The results and relationships were graphed and tabulated to identify optimum conditions or trends.

  During the course of the trials, the WKE plant continued to operate in a normal mode, which did not allow for absolute control of the feed quality during each of the continuous trials. The size and nature of the facility made it difficult to maintain steady state conditions, while varying one parameter of interest. However, the trends were readily identifiable and considerable knowledge was also obtained relating to the problems of full scale oxidizer operation.

- Special Considerations – During the course of the trials, an attempt was made to lower pH by premixing acid into the slurry in advance of the oxidation run. This resulted in the emission of noxious sulfur dioxide fumes, which were clearly not acceptable to workers down wind. For this reason, the addition of acid was limited to slurries above a pH of 4 and only during actual oxidation agitation.

  The presence of unreacted lime in the feed slurry was also found to be a significant factor influencing the demand for acid. The presence of unreacted lime or limestone in the feed slurry is a cost factor which must be controlled by the plant operations in their preparation and application of lime or limestone to the scrubber reactor. Depending on the feed chemistry, a pH increase (above 5.5) can quickly impede the oxidation process.

  After start-up, the oxidizer emissions are primarily water vapor. The level of sulfur species in the water vapor was not monitored, but was discernable during certain periods of the trial. Noxious fumes were readily detected, but generally dissipated with control of the reaction pH.

RESULTS

- Thickener Underflow Oxidation Rate - The highest batch rates for the TUF slurry were only a little higher than those measured under continuous feed conditions. The maximum batch rate with TUF slurry was 2.5 tph yielding 5.1 tph of gypsum. Neither of the rates was satisfactory and was less than half the rate warranted by EIMCO. The continuous rates were generally more reflective of the problems to be expected under normal operating conditions. The highest continuous oxidation rate for TUF slurry was 2.3 tph.

  A number of the early trials yielded apparently promising results which were misleading due to instrumentation problems and a limited understanding of the factors affecting the oxidation process. The inability to control the slurry chemistry resulted in high acid demand, and inlet air flow measurements did not accurately reflect the oxygen consumption. The ongoing design problem with oxygen mass transfer generally kept our focus on fixing the problem rather than fine tuning other factors at the low rates achieved. Subsequently, the effects of slurry concentration below 20%, small bubble generation, and feed chemistry were not well understood until subsequent tests were completed with a new oxidizer design by Synmat in 2003.

- Absorber Slurry Oxidation Rate – The highest rates were realized by oxidizing absorber slurry, which had a much lower level of unreacted lime. The slurry was collected in the tower before re-entering the reactor vessel. The AS batch rate ranged up to 3.4 tph yielding 6.0 tph of gypsum. This rate is not representative of steady state conditions. This oxidation rate also reflected the results of an increase in the rotor tip speed from 8 mps to 9 mps. AS continuous rates ranged up to 2.9 tph for the EIMCO Oxallizer, yielding 5.8 tph of FGD gypsum. The slurry was generally received at a lower pH and concentration than the TUF slurry.

- Acid Consumption Rate – The demand for acid was set by the pH of the reactor. Unfortunately, the pH correction was done in the oxidation vessel, and contributed to poor oxidation rates. The acid consumption varied widely, but was much higher for TUF slurry than for the absorber slurry used later in the trials. The acid consumption rate was over 5 gallon per ton of TUF oxidized, but only 2 gallon per ton of absorber slurry oxidized. This represented a considerable economic advantage for the utilization of absorber slurry over TUF slurry. The presence of unreacted lime and un-dissolved sulfites are the primary factors governing the acid demand. Under certain slurry feed conditions, absorber slurry was oxidized during extended continuous trials without the addition of acid.

- Equipment Response – The EIMCO oxidizer vessel showed no adverse effects from heat, abrasion, scaling or corrosion during the course of the trials. The Flender drive system performed at peak loading conditions for much of the trial and experienced no downtime. A wide range of slurry concentrations were agitated in the vessel with no problems resulting from solids settling during the recurring stoppages. Pumps, flowmeters, data collection systems, acid feed systems and automatic modulating valves all functioned dependably.

  However, the tank level sensor stilling well and the 14” exhaust stack were both removed in favor of a better a better design. The major limiting factor was determined to be the inability of the turbine to entrain air in the slurry. In an effort to address this problem, an axial fan was retrofitted to the air inlet to increase airflow into the turbine vortex. The measured air flow was doubled, but resulted in little improvement to the net oxidation rate.

- FGD Gypsum Quality – The purity of all the gypsum samples were above 93%. Processed and washed samples were 98+% pure. The crystal size varied greatly due to the nature of the trials, but was within the 10 to 150 micron range under steady state continuous operating conditions. The color was near white when washed with no streaking or clumping observed.

- Filtration – The FGD gypsum filtered well on a horizontal belt filter, and readily dewatered to a moisture level of 10%. The field trial did not allow for the installation of a properly sized filtration system, which resulted in a thicker cake than the 1 meter filter could properly dewater.

FINDINGS

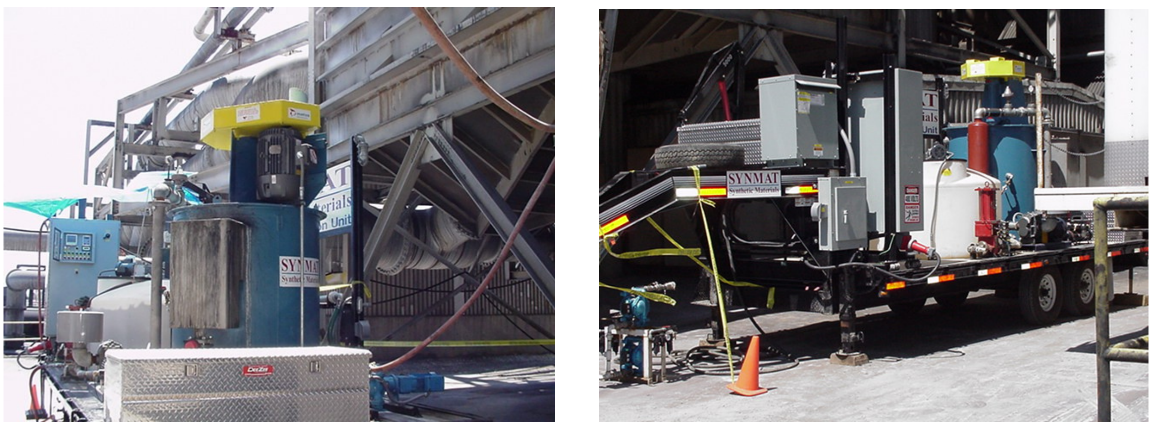
- Oxidation Rate – The economics of operation depends heavily upon the equipment oxidation rate. Various attempts to increase the oxidation rate met with little success.
    - Oxygen diffusion into the slurry is the critical feature in this design. The airflow into the oxidizer is not a good measure of the oxygen utilization for this unit, and was actually misleading. The optimum oxygen diffusion and oxidation rate was achieved at an operating level which brought the liquid vortex to the top edge of the rotor blade. The water sealed the air chamber and reduced the airflow at this level, but wetted the blade tip along the full length for cavitation.
    - Introducing forced air into the vortex assured that the pressure gradient would be favorable, but did not significantly improve the oxygen diffusion rate, and consequently the mass transfer rate of oxygen remained low.
    - The increase in the turbine tip speed had the effect of increasing the oxidation rate 10%. However the increase was achieved at a great increase in power consumption.
    - Reducing the slurry concentration below 15% appeared to have a beneficial effect on the overall oxidation rate. This was not substantiated, and may be the result of other factor in the slurry chemistry.

- Acid Consumption – The effect of feed slurry chemistry was demonstrated dramatically in the change from thickener underflow as the feed source. The absorber stack slurry was not contaminated by unreacted lime and contained an abundance of dissolved sulfites, unlike the TUF slurry. The dissolved sulfites act as free acid to the process which allows easy control of the critical pH level below 5.5. The utilization of the absorber stack feed slurry reduced the acid demand by more than half.

- Mechanism Recommendation – The trial results indicated that the oxygen dissolution into the slurry is the bottleneck to the reaction. A different mechanism must be used to provide the diffusion necessary to dissolve the oxygen into the slurry. A different design of turbine combined with an air injection system should be investigated further.

- Conclusion – The EIMCO oxidation equipment can produce high quality gypsum, but at a rate which is significantly lower than originally warranted. The utilization of TUF slurry is not feasible unless an economical source of acid can be utilized to produce a workable pH in the oxidizer.

- Outcome – A smaller demonstration unit was developed by Synmat to address the major design problems, and to provide trial results which are scaleable. Thus far, the results from 4 different trials have verified that the Synmat Oxidizer design is effective in achieving an oxidation rate which is more than double that of the EIMCO design.
  The 400 gallon mobile oxidation unit (MOxU) is completely portable, and has been successfully tested using 4 different feed slurry chemistries at three different sites. This prototype has been proven to provide the critical air diffusion in sulfite slurry sufficient to create a high oxidation rate. Below is the MOxU on site for a trial.



Photos of Synmat Mobile Oxidation Unit on Site for Trial

The design builds on two years of field experience in the oxidation of scrubber sulfites using turbine diffusion of injected low-pressure air supply. The MOxU features a VFD turbine motor and a variable flow, low pressure, air injection system which allows optimization of the power and air supply during the trial. The relatively small MOxU also allows for the testing of numerous trial feed conditions without incurring high capital expenditures. The unit is still restricted to acceptable pH, solids concentrations, and chemistry which affect all sulfite oxidation systems. However, several feed concentrations and sources have been combined in the feed tank to simulate actual options available at the plant.
  The Synmat oxidizer incorporates proven technologies into a new design with a wide application to the oxidation of sulfites. The trial requires no disruption to normal plant operations, and results can be quickly scaled up to a full-sized oxidizer vessel.

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