

## **Evaluation of Minnesota Taconite Wet Scrubbers at Minntac, Keewatin Taconite, Hibbing Taconite, and United Taconite**

by John Engesser, P.E.

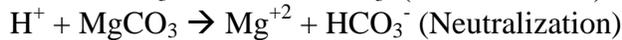
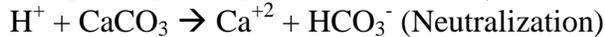
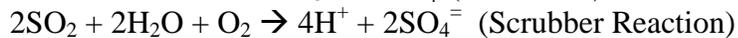
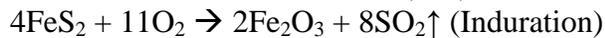
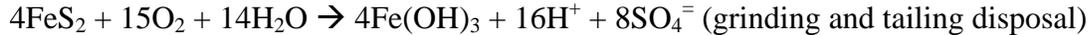
Minnesota Department of Natural Resources, Division of Lands & Minerals

This paper is a review of water treatment methods that can be used to increase sulfur dioxide scrubbing at Minntac, Keewatin Taconite, Hibbing Taconite, and United Taconite. The paper will look at the impacts that more efficient sulfur dioxide scrubbing will have on process water chemistry, tailing water chemistry, and iron oxide recovery.

### **Taconite Water Chemistry**

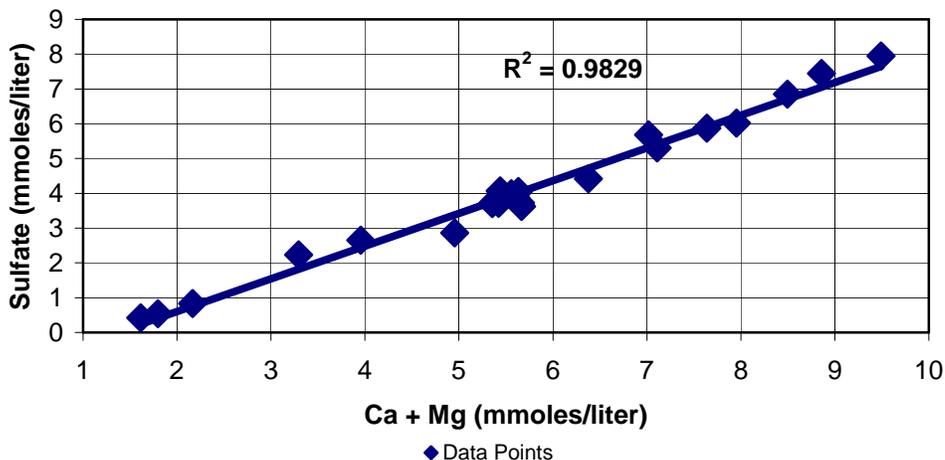
Minnesota taconite facilities have been operating for 40 to 50 years. During this time the concentration of dissolved solids in recycled process water and tailing water has increased. This increase in the ionic strength of taconite-process water has occurred because of the following four chemical reactions: 1) sulfide mineral oxidation and the subsequent formation of sulfuric acid, 2) the removal of soluble acid gases (sulfur dioxide, hydrogen chloride, hydrogen fluoride) from induration exhaust by wet scrubbers, 3) neutralization of acid gases by carbonate minerals, and 4) dissolution of soluble salts.

Sulfide minerals, present in taconite, oxidize and hydrolyze to form sulfuric acid when exposed to air and water during grinding and induration. Sulfuric acid is neutralized by calcium carbonate and magnesium carbonate, which are both present in taconite. These reactions cause an increase in the ionic concentrations of calcium, magnesium, and sulfate in process water and tailing water. The following reaction equations represent what occurs during grinding, induration and tailing disposal.



As the concentration of sulfate increases, the concentration of both magnesium and calcium increase. The following graph illustrates the correlation between hardness (calcium and magnesium) and sulfate in taconite process water.

**Sulfate Concentration Correlated to Calcium and Manganese Concentrations in  
Taconite Process Water**



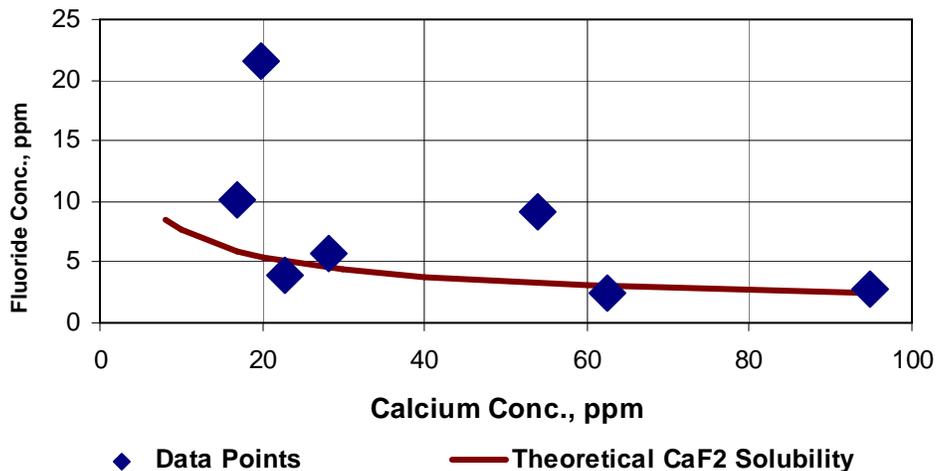
Increased sulfate concentration results in increased process water hardness, which can cause processing problems in flotation and balling. High calcium concentrations in process water results in precipitation of calcium carbonate in pipes. Calcium sulfate precipitation can also occur in certain areas of the plants when the calcium sulfate solubility limit is reached. The ultimate result of the increased water hardness is an increase in taconite production costs.

There are very few soluble salts present in taconite. However, with the advent of fluxed pellets, soluble chlorides (calcium, magnesium, sodium and potassium) are introduced into the water during fluxstone (calcite and/or dolomite) grinding. Chloride is volatilized during pellet induration and is subsequently removed by the wet scrubbers as hydrochloric acid. The following reactions represent the formation of hydrochloric acid during induration and the neutralization reactions that occur during scrubbing and after scrubbing.

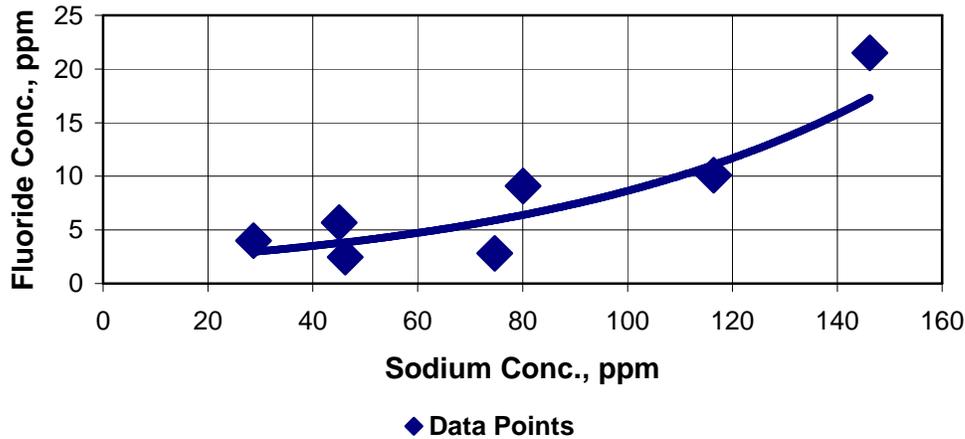


Small amounts of naturally occurring insoluble fluoride minerals (mostly fluorapatite) are present in Minnesota taconite. Approximately 90 to 95 percent of the fluoride is rejected to the tailings during magnetite concentration. The remaining fluoride (0.001% to 0.002% of the concentrate) enters the induration process. Fluoride minerals are also added to the concentrate with the addition of bentonite clay, limestone and dolomite prior to greenball formation. Approximately forty percent of the fluoride entering the induration process is volatilized during induration. The quantity of hydrogen fluoride that forms during induration increases as the concentration of sodium in the process water increases and the concentration of calcium in the process water decreases. Wet scrubbers remove the hydrogen fluoride that forms during pellet induration. Approximately 0.01 pounds of hydrogen fluoride dissolves in the process water for each ton of taconite processed. Most of the fluoride that dissolves in the process water precipitates as calcium fluoride. Fluoride concentration in process water is limited by calcium concentration because calcium fluoride is fairly insoluble in water and readily precipitates. The presence of sodium in process water aids in the dissolution of fluoride salts, which results in increased concentrations of fluoride in process water. The concentration of fluoride in taconite process water varies from 2 mg/liter to 25 mg/liter depending on the concentration of calcium and sodium. The following two graphs demonstrate how the concentration of fluoride in process water is affected by the concentrations of calcium and sodium in process water.

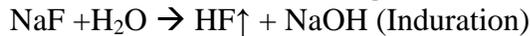
**Calcium and Fluoride in Process Water Samples from Minnesota Taconite Plants**



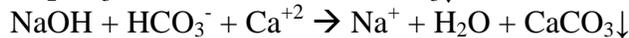
**Sodium and Fluoride in Process Water Samples from  
Minnesota Taconite Plants**



The following reactions represent the fluoride reactions that occur during induration and neutralization after scrubbing.



The addition of sodium carbonate and/or sodium hydroxide to taconite process water results in the precipitation of calcium carbonate, which decreases the concentration of calcium in the water. The following reactions represent what occurs when sodium carbonate and sodium hydroxide are added to taconite process water.



**Water Chemistry Conclusions**

- 1) Increased concentrations of sulfate in taconite process water results in increased concentrations of hardness (calcium and magnesium). This increased hardness results in increases in pellet production costs.
- 2) Sulfate and calcium will precipitate from solution once the solubility limit of calcium sulfate is reached. This will occur when the products of the molar concentration of calcium and sulfate reach the solubility limit. Sodium sulfate is extremely soluble.
- 3) Increased scrubber efficiency can result in increased sulfate concentration in taconite process water.
- 4) The concentration of sodium in taconite process water affects the amount of hydrogen fluoride that forms during pellet induration. Increased concentrations of sodium results in increased formation of hydrogen fluoride during pellet induration.
- 5) The concentration of calcium in taconite process water affects the amount of hydrogen fluoride that forms during pellet induration. Increased concentrations of calcium results in decreased formation of hydrogen fluoride during pellet induration.
- 6) The concentration of calcium in scrubber water affects the amount of fluoride that precipitates from solution after hydrogen fluoride scrubbing. Increased concentrations of

calcium results in increased precipitation of calcium fluoride and decreased concentration of fluoride in the taconite process water.

- 7) Precipitation of calcium fluoride and calcium sulfate can limit the amount of fluoride and sulfate that remain in solution in taconite process water.
- 8) The addition of sodium carbonate and sodium hydroxide to taconite process water decreases the concentration of calcium in taconite process water.

### **Past History of Taconite Process Water**

There are some observations that can be made by looking at past practices at Minnesota taconite facilities.

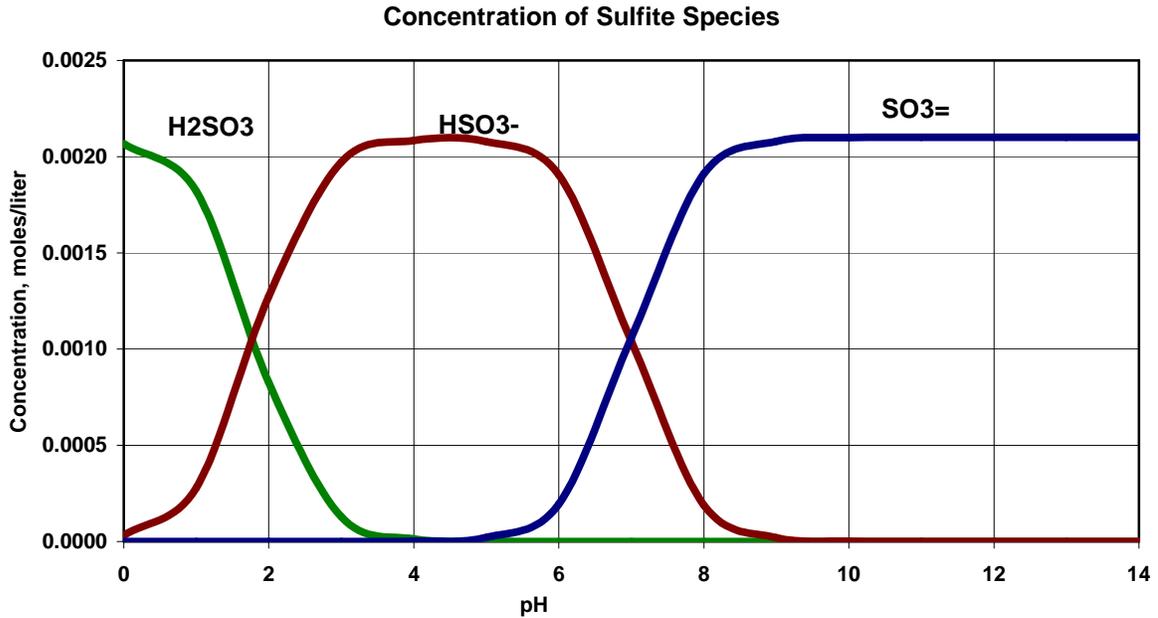
- 1) Two taconite facilities, Northshore Mining and LTV Mining used soda ash (sodium carbonate) water treatment to “soften” (precipitate calcium carbonate) process water. The tailing basins at these two facilities contain water that has the highest fluoride concentrations of all the Minnesota taconite facilities. Precipitation of calcium carbonate decreased the calcium concentration of the water, which decreased calcium fluoride precipitation; thus resulting in high fluoride concentration in the tailing water.
- 2) The tailing facility at Minntac contains the highest concentration of sulfate because Minntac installed four once through wet scrubbers, which remove sulfur dioxide. The sulfur dioxide is oxidized to sulfate. The tailing basin has no permitted direct discharge other than the existing seeps and so the sulfate concentration in the tailing water continues to increase due to the recycling of water from the tailing basin back to the scrubbers. Minntac has a lower fluoride concentration in tailing water than do most taconite facilities because of high calcium concentration, which limits the fluoride concentration to the solubility of calcium fluoride.
- 3) It appears that the lime re-circulating scrubber at Keewatin Taconite can limit the amount of sulfate and fluoride that enter the tailing water. This is accomplished by continually adjusting the scrubber water to the proper pH and allowing it to circulate until gypsum (calcium sulfate) and calcium fluoride precipitation occurs.
- 4) There is no precipitation reaction that limits the concentration of chloride in taconite process water.

### **Sulfur Dioxide Scrubbing at Taconite Plants**

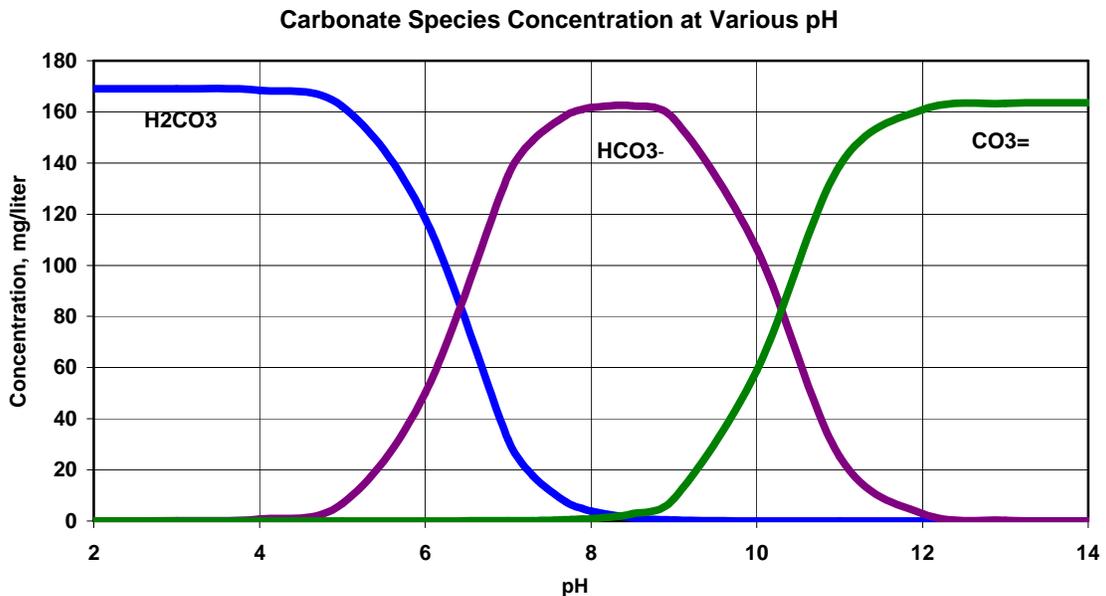
The efficiency of sulfur dioxide scrubbing in taconite induration scrubbers depends on the concentration of sulfur in the fuel and pre-fired pellet, the scrubber water chemistry, the scrubber water flowrate, the composition of the ash from the fuel, the composition of dust formed during pellet induration, and residence time (gas - water contact time and reaction rates).

- 1) Sulfur dioxide scrubbing efficiency is affected by the concentration of sulfur in the fuel and the pre-fired pellet. During pellet induration, the sulfur that is present in the fuel and pre-fired pellet oxidizes to sulfur dioxide. An increase in the amount of sulfur entering the furnace results in increased concentration of sulfur dioxide in the waste gas. Sulfur dioxide begins to react with the alkalinity in the scrubber water as the sulfur dioxide dissolves in the water. The alkalinity and the pH of the scrubber water begin to decrease as the sulfur dioxide reacts. As the pH of the scrubber water decreases, the rate of sulfur

dioxide scrubbing decreases. Once the pH of the scrubber water decreases to 4.5, the reaction of sulfur dioxide with bicarbonate is essentially complete. Sulfite ( $\text{SO}_3^-$ ) and bisulfite ( $\text{HSO}_3^-$ ) are much more stable in water than is sulfurous acid ( $\text{H}_2\text{SO}_3$ ). Sulfurous acid begins to form at about pH 4. Sulfur dioxide scrubbing that occurs below pH 4.5 is due to the solubility of sulfur dioxide in water, which is controlled by the partial pressure (concentration) of sulfur dioxide in the waste gas.



- 2) Sulfur dioxide scrubbing efficiency is affected by the alkalinity and pH of the scrubber water. The pH of taconite process water is usually very close to pH 8, which is the pH at which the maximum concentration of bicarbonate alkalinity occurs. As bicarbonate reacts with sulfur dioxide, the scrubber water pH decreases and the bicarbonate alkalinity decreases. Water that contains high bicarbonate alkalinity concentration is capable of scrubbing more sulfur dioxide than water that contains low bicarbonate alkalinity concentration.



- 3) The scrubber make-up water flowrate affects the amount of bicarbonate that enters the scrubber, which affects the amount of sulfur dioxide removed from the waste gas. Higher scrubber make-up water flowrates result in more bicarbonate alkalinity available to react with sulfur dioxide in the waste gas. The table below indicates that sulfur dioxide scrubber efficiency is dependent on the amount of bicarbonate alkalinity ( $\text{HCO}_3^-$ ) that enters the scrubber. Keewatin Taconite data is not included in the table below because most of the alkalinity in the scrubber water at Keetac comes from lime addition rather than the make-up water.

Taconite Plant	Scrubber Make-up, gpm	Make-up $\text{HCO}_3^-$ , lb/min	Make-up $\text{HCO}_3^-$ , lb mole/min	Reacted $\text{HCO}_3^-$ , lb mole/min	Remaining $\text{HCO}_3^-$ , lb mole/min	Calc. Water $\text{SO}_2$ Scrubber Efficiency	Calc. Air $\text{SO}_2$ Scrubber Efficiency
Minntac L6&7	2800	4.10	0.0672	0.0596	0.0077	60%	71%
Minntac L4&5	2800	4.10	0.0672	0.0288	0.0384	53%	
Utac L2	870	1.57	0.0257	0.0257	0.0000	26%	27%
Hibtac	3900	7.67	0.1258	0.0187	0.1070		75%

- 4) Sulfur dioxide scrubbing efficiency is affected by the neutralizing capacity of ash from the fuel. Coal ash contains little or no acid neutralizing capacity; however, wood ash contains large amounts of CaO and MgO, which will neutralize acid components in the waste gas. The ash content of wood is about 2% by weight. Following is a table that lists the ash analyses for northern Minnesota birch and aspen. Using the MgO and CaO analyses, the neutralizing capacity of the wood ash is about 0.44 moles per short ton of wood burned.

Wood	% $\text{Fe}_2\text{O}_3$	% $\text{SiO}_2$	% $\text{Na}_2\text{O}$	% $\text{K}_2\text{O}$	%CaO	%MgO	% $\text{SO}_3$	%LOI
Birch	1.30	0.85	8.70	15.1	45.8	11.6	3.1	13.5
Aspen	0.59	5.80	0.17	12.2	52.7	5.44	3.1	18.5

- 5) Sulfur dioxide scrubbing efficiency is affected by the addition of limestone to the pre-fired pellets. Taconite plants add from 1% to 10% limestone to pre-fired pellets depending on the type of pellet that is being produced. Limestone addition rates of 1% can be used for standard (acid) pellet production; whereas, limestone addition rates of 8% to 10% are used for fluxed pellet production. The taconite pelletizing process produces from 2 to 8 pounds of dust per gross ton of pellets produced. Wet scrubbers remove this dust from the waste gas. The acid neutralizing capacity of this "scrubber dust" during the production of a 1% limestone pellet is about 0.2 to 0.8 millimoles for each ton of standard pellets produced. The acid neutralizing capacity of "scrubber dust" during the production of 10% limestone pellets is about 2 to 8 millimoles for each ton of pellets produced.

The following table indicates some calculated sulfur dioxide scrubber efficiency rates. Two efficiency rates are listed in the table. The first scrubber efficiency rate was calculated using the increase of sulfate in scrubber water. The second scrubber efficiency rate was calculated using the concentration of sulfur dioxide in the waste gas entering the scrubber (calculated from mass balance) and the concentration of sulfur dioxide exiting

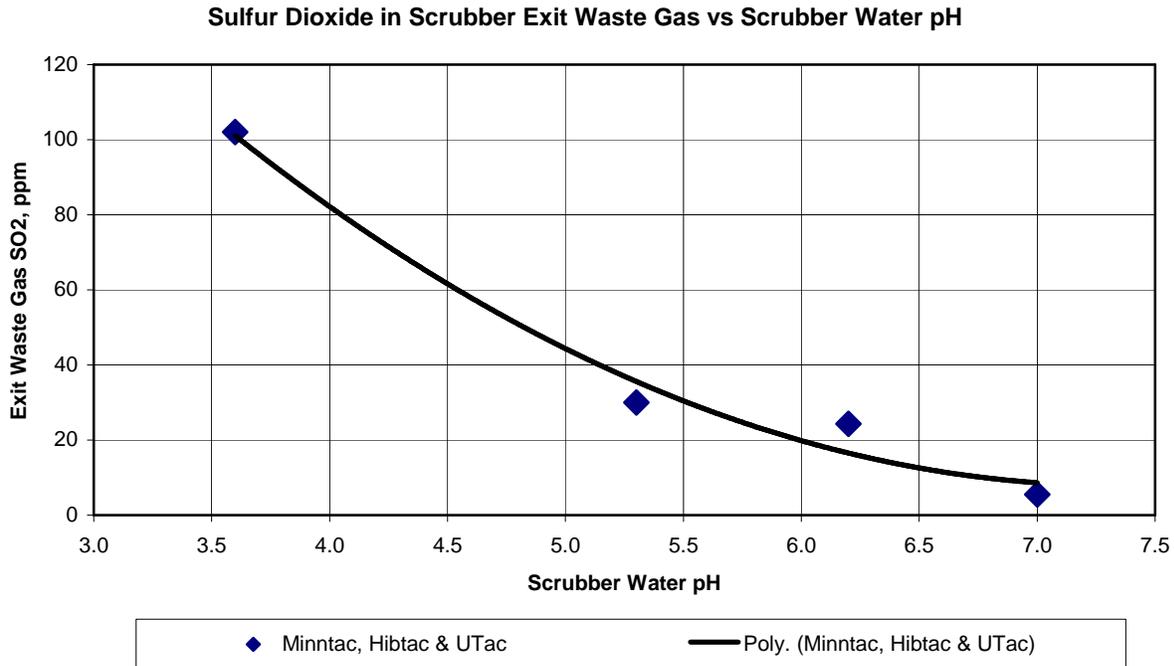
the stack. The sulfur dioxide removed by the dust was calculated based on a calculated removal rate for bicarbonate alkalinity by the scrubber water that occurred from pH 8 (pH of taconite process water) to the measured pH of the scrubber exit water (listed in the table). The difference between the total sulfur dioxide removal (efficiency) and the sulfur dioxide that reacted with the bicarbonate alkalinity in the water is the amount of sulfur dioxide that reacted with the dust. Notice that for Minntac Lines 4 & 5 the amount of sulfur dioxide removed by the “scrubber dust” was more than any other scrubber listed in the table. This is because wood was used as a fuel and wood ash has a very fine grain size and is therefore very reactive. This data demonstrates that sulfur dioxide scrubber efficiency is dependent on neutralization of scrubber water by the dust and fuel ash.

Taconite Plant	Waste gas acfm, 110°F	Pellet Prod lb/hr	SO2 ppm	Nat Gas scfh	Coal lb/hour	Wood lb/hr	Pellet Type	lb SO2 minute	Calc. Water SO2Scrubber Efficiency	Calc. Air SO2 Scrubber Efficiency	Scrubber Water pH	SO2 Scrubbing by dust
Keetac	613,789	693	62.9	76,200	20,175	0	Acid	5.94	50%		6.4	NA
Minntac L6&7	407,951	415	88.0	83,900	16,500	0	Flux	5.53	60%	71%	5.3	20%
Minntac L4&5	404,883	415	51.6	136,950	0	11,450	Flux	3.21	53%		6.2	35%
Utac L2	583,428	452	139.7	0	15,325	0	Acid	12.54	26%	27%	3.6	15%
Hibtac	468,871	384	21.9	96,260	0	0	Acid	1.58		75%	7.0	39%

Note: Waste gas flowrates are calculated using, the oxygen content of the waste gas, fuel type, fuel composition, fuel rate, pre-fire pellet moisture, and pre-fired pellet combined water and carbon dioxide content with the assumption that all combustion products are water and carbon dioxide.

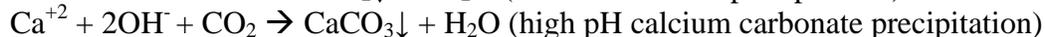
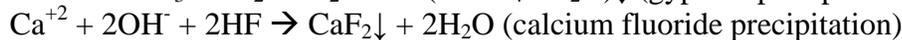
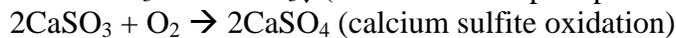
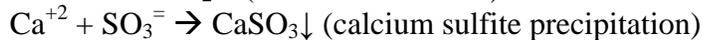
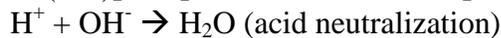
- 6) Liquid gas reactions are dependent on the gas concentration that is in contact with the liquid. As the gas concentration decreases, the liquid gas reaction rate decreases. In the case of sulfur dioxide scrubbing the gas is sulfur dioxide and the liquid is water. The following table indicates the concentrations of sulfur dioxide in the taconite waste gas leaving the scrubber (gas after scrubbing). Notice the high pH in the Hibtac scrubber water and the amount of alkalinity remaining in the water that is still available to react with sulfur dioxide. However, the sulfur dioxide concentration in the waste gas is very low (5.5 ppm) and, therefore, the reaction is very slow. The graph below indicates that there is a sulfur dioxide concentration limit that is attainable in a wet venturi scrubber due to such things as residence time and scrubber water flowrate.

Taconite Plant	Scrubber Water pH	Scrubber Exit SO2 ppm	Remaining HCO3- lb mole/min
Keetac	6.4	31.1	NA
Minntac L6&7	5.3	30.0	0.0077
Minntac L4&5	6.2	24.3	0.0384
Utac L2	3.6	102.0	0.0000
Hibtac	7.0	5.5	0.1070

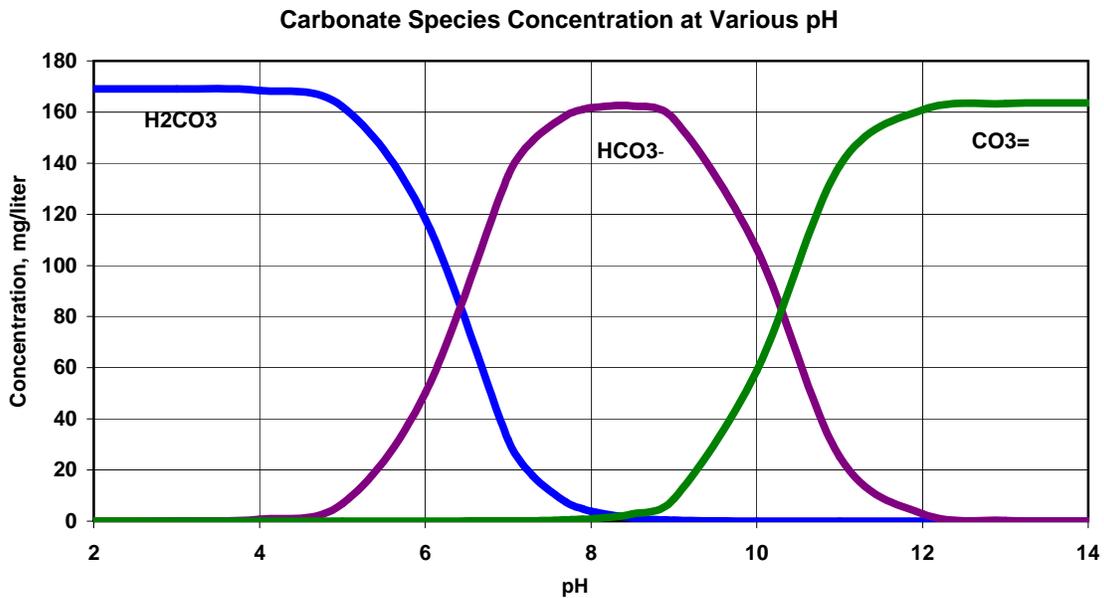
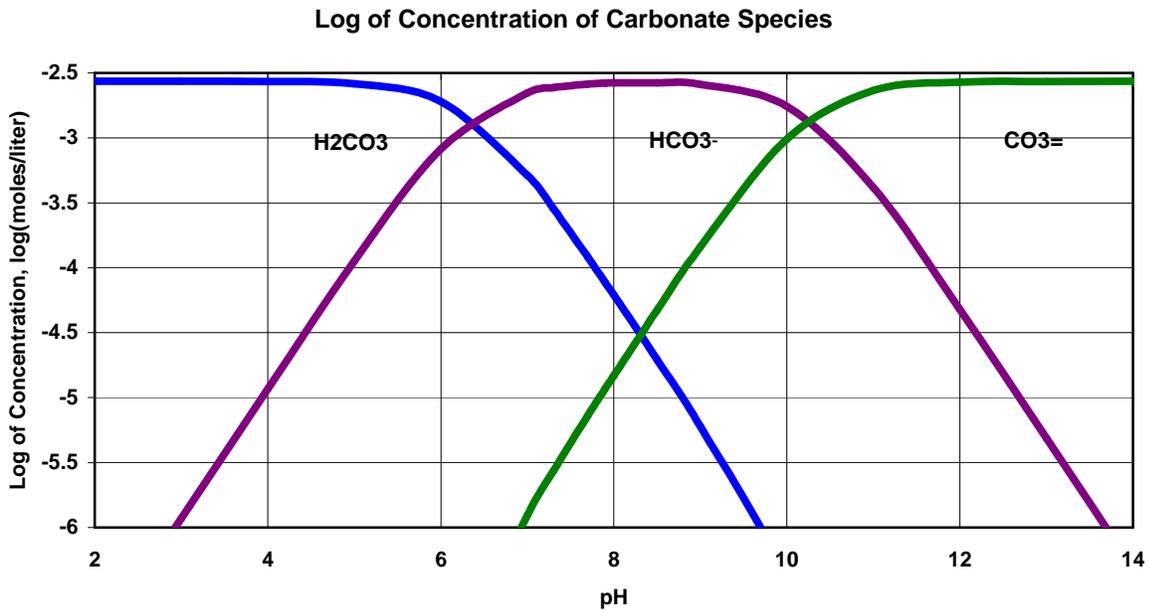


### Lime Scrubber Reactions (Re-circulating Lime Scrubber)

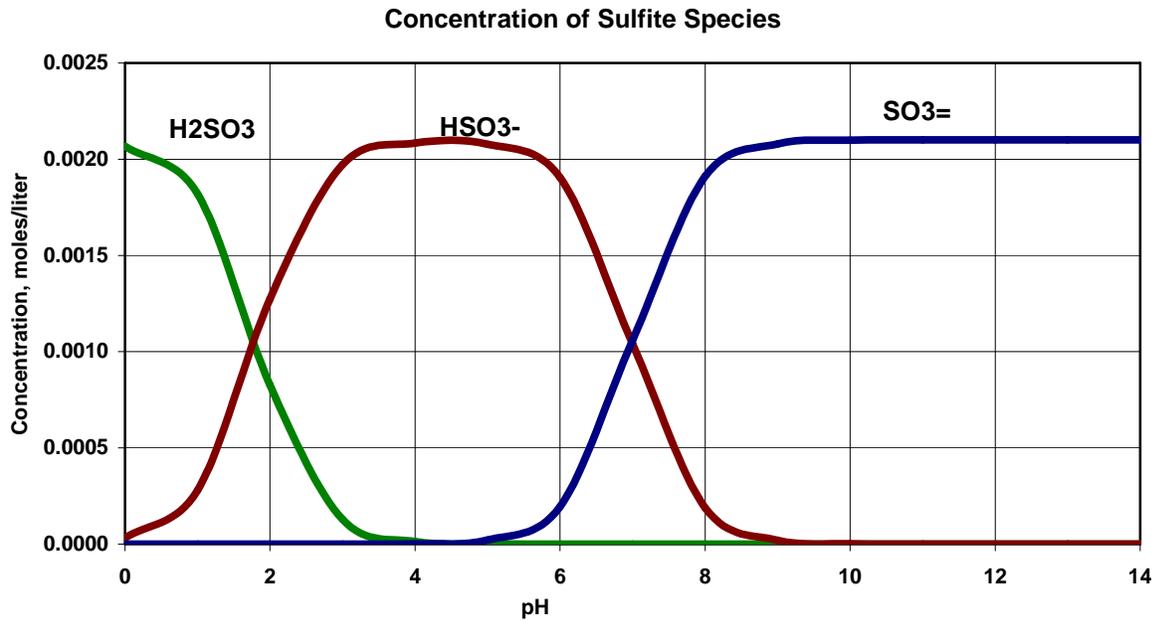
Scrubber Reactions with hydrated lime (calcium hydroxide)



The addition of lime to scrubbers increases acid gas scrubbing efficiency. As the pH of the scrubber water increases, the amount of acid gas removed from the waste gas increases. However, the pH of the scrubber water cannot be increased to the point where bicarbonate and/or carbon dioxide are converted to carbonate because calcium carbonate will precipitate from solution and scaling within the scrubber will occur. As pH increases, the hydroxide (from lime addition) that is present in the scrubber water removes carbon dioxide from the waste gas and converts it to carbonate, which then precipitates as calcium carbonate. Calcium carbonate precipitation will plug scrubbers, which in turn decreases scrubber efficiency. The following two graphs depict the concentration of carbonate at various pH. These graphs are based on water that has a concentration of 120 mg CO<sub>2</sub>/liter. Depending on pH the CO<sub>2</sub> can be carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and/or carbonate (CO<sub>3</sub><sup>=</sup>).



The above two graphs indicate that as the pH of the water in a re-circulating lime scrubber increases, the concentration of the carbonate ion increases. The carbonate concentration must be maintained at a low enough concentration that will not result in large amounts of calcium carbonate precipitation. The solubility product for calcium carbonate is  $4.9 \times 10^{-9}$ . A re-circulating scrubber that operates at 100F and maintains the sulfate concentration in the water at 1400 mg SO<sub>4</sub>/liter will have water that has a calcium concentration of 650mg Ca/liter. This means to maintain a calcium carbonate precipitation rate of less than 1 mg/liter, the concentration of carbonate has to be less than  $10^{-5}$  moles/liter. Examining the log graph above, the pH of the re-circulating scrubber water should be maintained at a pH less than 7.5 to ensure the carbonate concentration is less than  $10^{-5}$ .



The solubility of calcium sulfite is less than the solubility of calcium sulfate. The above graph indicates that the concentration of bisulfite ( $\text{HSO}_3^-$ ) is greater than the concentration of sulfite when the pH of the scrubber water is less than 7. If the sulfite oxidation rate to sulfate is not rapid enough, then calcium sulfite can precipitate from solution, especially when the pH of the scrubber water is above 7. High concentrations of sulfur dioxide in the waste gas can result in high enough concentrations of sulfite in the scrubber water that precipitation of calcium sulfite can even occur as low as pH 6. Calcium sulfite precipitation in the scrubber can cause scaling and plugging problems. For this reason it is difficult to operate re-circulating-lime scrubbers at a pH that is above 7 without decreasing scrubber efficiency by forming precipitates.

#### Application to Minnesota Taconite Induration Scrubbers

**Keewatin Taconite Scrubber** – Keewatin Taconite has a re-circulating-lime, venturi-rod scrubber. In order to maintain maximum sulfur dioxide scrubber efficiency, the scrubber should be operated between pH 7 and pH 7.5. If it is operated at a pH greater than 7.5, calcium carbonate and calcium sulfite scaling will occur in the scrubber, which will result in decreased scrubber efficiency and could even result in shutting down the process to clean the scale formation from the scrubber. It would appear that Keewatin Taconite is currently operating at near optimum sulfur dioxide scrubbing conditions.

**Minntac Line 3 Scrubber** – Minntac installed a re-circulating-lime venturi-rod scrubber on the Line 3 pellet induration furnace during 2005 - 2006. Minntac is currently not operating Line 3; however, when Line 3 was operating, scaling in the scrubber was a problem. The scrubber system will have to be optimized to ensure good sulfur dioxide scrubbing without scaling. When this optimization is accomplished, Line 3 should have sulfur dioxide scrubber efficiency similar to the Keewatin Taconite re-circulating lime scrubber.

**Minntac Lines 4, 5, 6 and 7 Scrubbers** – Minntac has “once through” venturi-rod scrubbers on lines 4, 5, 6, and 7 pellet induration furnaces. It is currently estimated that approximately 70% of the sulfate in the Minntac basin water is due to sulfur dioxide scrubbing. The wet scrubbers are currently removing more than 50% of the waste-gas sulfur dioxide when Minntac is producing fluxed pellets and/or using wood as a fuel. Minntac produces fluxed pellets on lines 6 and 7 using coal and natural gas as fuel. This combination (fluxed pellets, coal and natural gas) results in a sulfur dioxide scrubbing efficiency that is greater than 50%. Minntac produces standard (acid) pellets and fluxed pellets on lines 4 and 5 using wood and natural gas as fuel, which results in a sulfur dioxide scrubbing efficiency greater than 50%. These scrubber efficiencies will not be improved by adding chemicals to increase scrubber water alkalinity or by installing a re-circulating lime scrubber similar to the Keewatin Taconite Scrubber.

**Hibbing Taconite Company** – Hibbing Taconite Company (Hibtac) has three furnace lines with “once through” venturi rod scrubbers. Hibtac does not use coal as a pellet induration fuel. This means that the only sulfur entering the waste gas is from the taconite greenballs (pre-fired pellets). The calculated concentration of sulfur dioxide in the waste gas entering the scrubber is about 25 ppm. The concentration of the waste gas leaving the scrubber is about 6 ppm. The scrubber water leaving the scrubber still has a pH of 7 and contains 200 ppm bicarbonate alkalinity. This means that the sulfur dioxide scrubbing reaction is gas concentration limited, which also means that sulfur dioxide scrubbing efficiency will not be improved by adding chemicals to increase scrubber water alkalinity. The data also show that the installation of a re-circulating lime scrubber similar to the Keewatin Taconite Scrubber will not improve scrubbing.

**United Taconite** – Line 2 at United Taconite (Utac) has two re-circulating venturi rod scrubbers. The scrubber water from each scrubber is sent to two small thickeners. The underflow from each thickener is pumped back to the process at a rate of 435 gpm or a total of 870 gpm for the two scrubber systems. The overflow from the scrubber thickeners is sent back to the scrubbers with fresh make-up water. The make-up water is equal to the blowdown plus evaporative losses. The bicarbonate alkalinity entering the scrubber water is equal to the amount of bicarbonate alkalinity present in the make-up water. This limits the amount of sulfur dioxide that is removed from the waste gas to the amount of sulfur dioxide that will react with the bicarbonate alkalinity in the make-up water plus the amount that will react with the dust plus a small amount of soluble sulfur dioxide. This operating practice limits the amount of sulfate that enters the process water and the tailing water. The concentration of sulfate in the scrubber water currently increases from about 250 mg/liter to 800 mg/liter. This means that 4.0 pounds of sulfate per minute enters the process water (tailing water) with a scrubber blowdown rate of 870 gpm. The acid neutralization for the blowdown water comes from calcium and magnesium carbonates present in the ore, which limits the solubility of fluoride through calcium fluoride precipitation. Increasing the alkalinity of the water that is re-circulated from the scrubber thickener to the scrubber would increase sulfur dioxide scrubbing efficiency.

Following are some scenarios that could be considered to increase the sulfur dioxide scrubbing efficiency for Line 2 at United Taconite:

- 1) Increasing the alkalinity of the scrubber water by adding sodium hydroxide or sodium carbonate to the current system would increase sulfur dioxide removal. Addition of either of these chemicals would increase sulfur dioxide removal, but it also would result

in increased sulfate and fluoride concentrations in the tailing water. Doubling sulfur dioxide scrubbing efficiency by using either sodium hydroxide or sodium carbonate will result in an addition of 8.0 pounds of sulfate per minute to the tailing water (double the current rate). The current process water at United Taconite is 225 to 250 mg/liter. Doubling the sulfate input would result in sulfate concentrations of 450 to 500 mg/liter in the process water. Addition of sodium salts would also result in fluoride concentrations in the process water (tailing water) that could reach 20 mg/liter. Use of these salts will result in increased concentrations of both fluoride and sulfate in tailing water, which would create environmental problems with the tailing water.

- 2) Lime addition to the scrubber water will increase sulfur dioxide scrubbing efficiency and will also limit the amount of sulfate and fluoride in the tailing water by precipitation of calcium sulfate and calcium fluoride. However, lime addition could not be used with the current scrubber design. Adding lime to the current system would result in scaling problems, which would result in decreased sulfur dioxide and particulate scrubbing efficiency. The current scrubbers and water handling system would have to be redesigned to allow for lime addition to the scrubber water.
- 3) The installation of a new re-circulating lime scrubber similar to the Keewatin Taconite scrubber system would result in increased sulfur dioxide scrubbing efficiency. This type of scrubber would nearly double the current sulfur dioxide scrubbing efficiency. The result would be the removal of an additional 2.8 pounds of sulfur dioxide per minute (700 tons per year at 95% operating time). A scrubber blowdown rate of 350 gallons per minute would be required in order to maintain the current rate at which sulfate enters the tailing water (4.0 pounds per minute). One of the variables that must be considered when designing a re-circulating scrubber is the solid concentration in the water that is circulated back to the scrubber. If the solids concentration is too high, the efficiency of the scrubber can be affected and the amount of blowdown has to be increased to keep the solids at the proper concentration. A blowdown rate of 350 gpm should work if a dust collector, such as a multiclone system, is installed prior to the scrubber; however, if dust collection cannot be installed prior to the scrubber, the blowdown rate would probably have to be about 700 gpm. A scrubber blowdown rate of 700 gpm would not result in the precipitation of calcium sulfate and, therefore, the amount of sulfate entering the tailing water would be about 8 pounds per minute. This would result in doubling the amount of sulfate that is currently entering the water (4 lb/min to 8 lb/min).

The installation of a re-circulating lime scrubber without dust collection prior to the scrubber would result in a system that would require a blowdown of about 700 gallons per minute. This would result in doubling the current concentration of sulfate and calcium in the process water. The calcium concentration in the process water will increase because lime will neutralize the acid gases present in the scrubber water. The sulfate concentration and the calcium concentration of the process water would increase to about 500 mg/liter and 160 mg/liter respectively. This increase in hardness would result in operating problems that would be difficult to predict. It will be difficult to determine the costs associated with the resulting increase in hardness and sulfate concentrations. Some of the problems that would occur are:

- a) Increased scaling in plant process pipes due to increased concentrations of calcium. The process water will essentially be saturated in calcium carbonate. Calcium carbonate precipitation will occur in pipes. It will also occur on mineral surfaces during grinding when water temperatures increase.
- b) Calcium carbonate precipitation on mineral surfaces can have a negative impact on magnetite recovery. The resulting increase in the loss of magnetite ore to the tailings will increase the cost of production.
- c) Currently United Taconite does not have flotation, but calcium carbonate precipitation on mineral surfaces has a negative impact on the flotation process, which results in additional flotation reagent consumption.
- d) Increased calcium concentration in process water results in a deterioration of pre-fired pellet quality that is corrected by increasing pre-fired pellet moisture and increasing binder use. United Taconite uses organic binders. Past research with bentonite clay indicates that an increase of 10 mg/liter in calcium and/or magnesium (hardness) in the process water results in a 3% increase in bentonite clay consumption in order to maintain pre-fired pellet quality. The current Ca+Mg concentration in United Taconite process water is 80 mg/liter. An increase to 160 mg/liter (double the current concentration) would result in at least a 24% increase in binder use. Organic binders are usually affected more by water chemistry than is bentonite clay, which means the use of organic binder would increase by at least 24% and/or the current organic binder might no longer work.
- e) The scrubber thickener underflow solids currently are sent back to the process. This results in approximately 80 to 100 pounds of taconite concentrate per minute, which is equivalent to approximately 25,000 long tons of pellets per year. The result would be that if multiclone dust collectors cannot be installed prior to the wet scrubber. A production loss of approximately 25,000 long tons of pellets per year would occur.

Dust collectors prior to wet scrubbers would be necessary to maintain the current process water quality. The following items would have to be considered when evaluating an installation of a re-circulating lime scrubber system with dust collection prior to the wet scrubbers at United Taconite:

- a) Installation of multiclones to collect about 20,000 long tons of concentrate per year will be needed. A system to recycle the multiclone dust back into the pellet process will also need to be evaluated. It does not appear that there is enough room in the pellet plant to install multiclones prior to the current wet scrubbers. An evaluation will have to be made to determine if the installation of multiclones is possible.
- b) A re-circulating lime scrubber retrofit installation would probably require a new building because all of the necessary equipment would not fit into the confines of the current pellet plant. The new building would have to contain a lime mixing facility, a scrubber recirculation tank, a lime addition system with pH controls, a scrubber water solids thickener for the blowdown water treatment, and a filtering system to filter the solids. An alternative to a filtering system would be a lined settling pond.

- c) The filtering system would have to be sized for 20 short tons per day if multiclones are installed.
- d) The current venturi rod scrubbing system would have to be evaluated to determine if a new rod design is needed to handle the increased solid load that would occur with the re-circulating lime scrubber.
- e) An evaluation of increased operating costs associated with a re-circulating lime scrubber would also be needed. These should include
  - i. Ore losses associated with the dust loss that will occur due to the loss of reclaimed ore dust. This would be about 5,000 long tons per year if pre-scrubber dust collectors (multiclones) are installed.
  - ii. Approximately 2500 short tons of lime per year will be needed to neutralize the scrubber water to pH 7.
  - iii. There will be approximately 8500 short tons of solids per year that will have to be filtered and hauled to a lined landfill or deposited in a lined settling pond. This will include 5600 short tons of dust, 2500 short tons of gypsum and 400 short tons of calcium fluoride. This would require 2 trucks per day to haul the material to a landfill.

#### References:

1. Engesser, J. "Effect of water chemistry, water treatment and Blaine on magnetite filtering and magnetite agglomeration with bentonite clay." Minerals & Metallurgical Processing. Vol 20, No. 3, August 2003.
2. Engesser, J. "Reduction of fluoride dissolution during induration off-gas scrubbing." Minerals & Metallurgical Processing. Vol 22, No. 1, February 2005.
3. Engesser, J. "Effect of Plant Process Water Chemistry on Silica Flotation and Balling", University of Minnesota Coleraine Minerals Research Laboratory, Iron Ore Cooperative Research Program -Minnesota Department of Natural Resources, 1994.
4. Engesser, J. "The Removal of Sulfate and Fluoride from Process Water – The Effect of Water Chemistry on Filtering and Flotation" University of Minnesota Coleraine Minerals Research Laboratory, Iron Ore Cooperative Research Program -Minnesota Department of Natural Resources, 1998.
5. Engesser, J. "Taconite Process Water and Tailing Water Quality – Cationic Exchange Effect on Balling and Flotation", University of Minnesota Coleraine Minerals Research Laboratory, Iron Ore Cooperative Research Program -Minnesota Department of Natural Resources, 1999.
6. Engesser, J. "Bentonite Quality – The Effect of Water Chemistry and Antifreeze Agents on Bentonite Binding Characteristics" University of Minnesota Coleraine Minerals Research Laboratory, Minnesota Technologies Inc, 2000.
7. Engesser, J. "The Reduction of Fluoride Dissolution during Induration Off-gas Scrubbing" University of Minnesota Coleraine Minerals Research Laboratory, Iron Ore Cooperative Research Program -Minnesota Department of Natural Resources, 2001.
8. Goetzman, H., Bleifuss, R., Engesser, J. "An Evaluation of Organic Binders as Substitutes for Bentonite Pelletizing", Proceedings of the 61<sup>st</sup> Annual Meeting of the Minnesota Section AIME and 49th Annual Mining Symposium, January 1988.

8.. Stone, R.L. "Relationship Between Zeta Potential of Bentonite and the Strength of Unfired Pellets", America Institute of Mining Metallurgical and Petroleum Engineers Society of Mining Engineers of AIME Transactions Volume 238, 1967.

9. Engesser, J. Minntac Agglomerator Sulfur Balance, 1994.

10. Engesser, J. Eveleth Taconite Agglomerator Sulfur Balance, 1998.

11. Engesser, J., Niles, H., "Mercury Emissions from Taconite Pellet Production", University of Minnesota, Duluth Natural Resources Research Institute, 1997.

12. Berndt, M., Engesser, J., "Mercury Transport in Taconite Processing Facilities: (I) Release and Capture During Induration" Iron Ore Cooperative Research Program – Minnesota Department of Natural Resources, 2005.

13. Benner, B., "Mercury Removal from Induration Off-Gas Wet Scrubbers", Environmental Cooperative Research Program – Minnesota Department of Natural Resources, 2001.