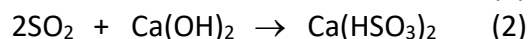
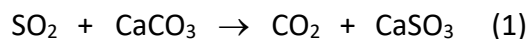


2.5) THE CHEMISTRY OF FLUE GAS DESULFURIZATION

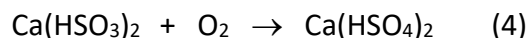
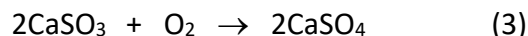
Objective: In this laboratory exercise you will evaluate the chemical properties of sulfur dioxide. You also will investigate the effectiveness of different “scrubber media” used to reduce sulfur emissions. Finally, you will compare different techniques for the oxidizing the scrubber byproduct in order to produce “artificial” gypsum, which serves as a substitute for the natural gypsum used in road construction and drywall.

Introduction: Sulfur dioxide is a major component of industrial air pollution. This pungent gas is not only implicated in a wide range of respiratory illnesses, it is also one of the main causes of acid rain. The use of tall chimneys for wider dispersal of sulfur dioxide gives some relief to people who live or work in these locations, but this does not remove the sulfur dioxide that causes acid rain. This problem is addressed with the installation of a smokestack scrubber.

In most scrubbers, the fumes pass through a “liquid filter” made up of an aqueous slurry of calcium carbonate and calcium hydroxide. This suspension is sprayed in a fine mist to maximize contact with the gas. This results in the production of both calcium sulfite and calcium bisulfite:



During flue gas desulfurization, some of the calcium sulfite and bisulfite "sludge" product is oxidized by the air into calcium sulfate and calcium bisulfate:



The calcium bisulfate produced in reaction 4 is easily converted into calcium sulfate by addition of a strong base:



This final product is often referred to as "flue gas desulfurization gypsum". It is used as a substitute for mined gypsum in a wide variety of applications such as filler material in drywall and cement. However, in order for the scrubber by-product to be approved for commercial use all of the sulfite must be oxidized. This is usually accomplished by thorough aeration of the sludge.

Note: Procedures A, B, and C are modified from lab activities that are presented in “Microscale Gas Chemistry” by Bruce Mattson, Susan Mattson, and Michael P. Anderson (Educational Innovations, 2006). They are being used here with the permission of the main author.

WARNING: Sulfur dioxide is both corrosive and toxic. Be sure to perform all procedures involving the production or transfer of sulfur dioxide under a functioning hood. Procedure A is particularly dangerous because accidents involving the spattering of acid or escape of gas are common. When you are finished with any syringe that comes in contact with this gas, remove all traces of sulfur dioxide by soaking it in a large beaker of 0.25-0.5 M sodium hydroxide. Sodium hydroxide solution is caustic, so be sure to flush with water any solution that comes in contact with your skin. At the end of the lab period, pour the solution down the drain and rinse off all traces of the sodium hydroxide.

Procedure A: Gas Preparation (To be carried out by the instructor):

WARNING: 6M HCl is very corrosive. Flush with running water for 5 minutes if it comes in contact with the skin. Wear goggles, lab apron, and closed-toed shoes because the gas pressure has been known to push out the plunger and splatter acid to the surroundings (including the face).

- 1) Put on your goggles and lab apron. Use the vial cap to weigh out about 1 gram of sodium bisulfite.
- 2) Use forceps to place the vial cap *carefully* into a *dry* 60-mL syringe (Fig. 1). If any of the crystals fall outside the vial cap, start over with a fresh syringe.
- 3) *Slowly* insert the plunger until it nearly touches the cap (Fig. 2). If any of the crystals fall outside the vial cap, start over with a fresh syringe.
- 4) Go to the fume hood and *very carefully* draw up about 5 mL of 6M HCl into the syringe *without letting any of the acid touch the crystals* (Fig. 3).



Fig. 1



Fig. 2



Fig. 3

- 5) *Immediately* cap the syringe so no gas can escape (Fig. 4). *This is the trickiest part of this procedure because the vial cap may sink below the surface before the syringe cap is in place.* Rinse the acid off the syringe when the cap is in place by dipping it into a large beaker of water.
- 6) Shake the syringe so that the acid and crystals make full contact (Fig. 5). This will cause the plunger to push outwards as gas is released.
- 7) Use your hand to make sure the plunger does not pop out completely (Fig. 6).



Fig. 4



Fig. 5



Fig. 6

- 8) Hold the capped syringe upright so that the heavier-than-air sulfur dioxide does not pour out (Fig. 7). **WARNING:** *It is critical that the next step be carried out under a functioning hood because the newly produced gas will be under pressure. Some will escape as soon as you open the cap.*
- 9) Open the cap and immediately connect this syringe to another syringe that has 2-3 inches of aquarium tubing connected to the nozzle as indicated (Fig. 8). *If you smell the gas escaping the hood, cap the syringe and leave the hood area until the smell is gone.*

- 10) Keep the first syringe upright so that the acid does not pour into the second syringe (Fig. 8). Slowly transfer all the gas to the second syringe by pushing in the plunger of the first syringe while pulling out the plunger of the second syringe.

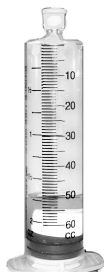


Fig. 7



Fig. 8

- 11) You should now have about 55-65 mL of sulfur dioxide in the second syringe. Cap this syringe and immediately soak the first syringe in dilute sodium hydroxide solution (according to the safety instructions at the start of this lab exercise). The solution remaining in this first syringe should be injected into a separate beaker of dilute sodium hydroxide before it is poured down the drain. To minimize the escape of sulfur dioxide fumes, *be sure to place the nozzle underwater* while you are doing this.

Procedure B: Discoloration of fruit pigments

- 1) Put on your goggles. Insert a piece of strawberry or radish into a 60-mL syringe and insert the plunger so there is just enough space for the item, but it is not crushed (Fig. 9).
- 2) Go to the fume hood and use aquarium tubing to transfer about 30-40 mL of sulfur dioxide to this syringe (Fig. 10). Steps 9-10 of *Gas Preparation* (Procedure A) describes gas transfer in more detail.
- 3) Note the color in 30-60 minutes. Leave it overnight and note the final color.
- 4) Soak both syringes in dilute sodium hydroxide solution (according to the safety instructions at the start of the lab exercise).



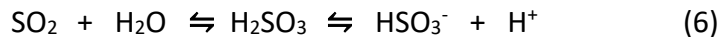
Fig. 9



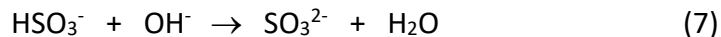
Fig. 10

Procedure C: Colorimetric Evaluation of Aqueous Sulfur Dioxide

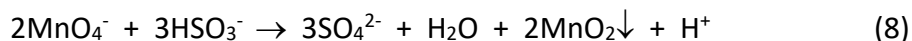
When sulfur dioxide is dissolved in water, this gas forms an equilibrium mixture with sulfurous acid, bisulfite ions, and hydrogen ions:



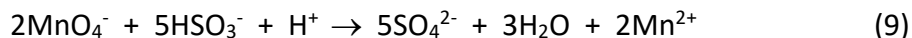
In basic solution, bisulfite is converted to sulfite:



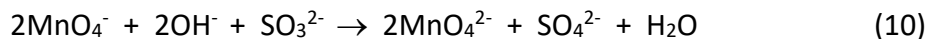
Because the central atom in these ions is not fully oxidized, both sulfite and bisulfite have significant reducing properties. This is why sulfur dioxide is used as a bleaching agent for the production of writing paper. The presence of sulfite and bisulfite ions can be detected by using the permanganate ion. When potassium permanganate is added to bisulfite in neutral solution, the solution loses its purple color and a brown precipitate of *manganese dioxide* is produced:



In acidic solution permanganate is converted into the *manganous* ion, which is nearly colorless:



In basic solution permanganate is converted into the *manganate* ion, which is green:



WARNING: *Aqueous sulfur dioxide is both corrosive and toxic. Potassium permanganate is a strong oxidizer. Be sure to flush with water for one minute if either solution comes in contact with your skin.*

- 1) Put on your goggles. Use a 60-mL syringe to draw up 10 mL of distilled water. Connect about 3 inches of aquarium tubing to the nozzle of the syringe. Go to the fume hood.
- 2) Remove the cap from a syringe containing 30-60 mL of SO_2 and immediately connect it to the syringe with the 10 mL water (Fig. 11). Transfer all the gas to this syringe. Steps 9-10 of *Gas Preparation* (Procedure A) describe gas transfer in more detail.
- 3) Cap the syringe (Fig. 12) and shake it for about 20 seconds so that the water in the syringe is saturated with this gas. This gas is very water-soluble, so there should be a significant decrease in the total volume of gas in the syringe.
- 4) Add 5 drops of water from the syringe to each of two incubation wells (Fig. 13).



Fig. 11



Fig. 12



Fig. 13

- 5) Add one drop of pH indicator to one of your two wells containing gas-saturated water as indicated (Fig. 14). Note the color

- 6) Add 1 drop of dilute potassium permanganate solution to the other well containing gas-saturated water (Fig. 15). Note the color.

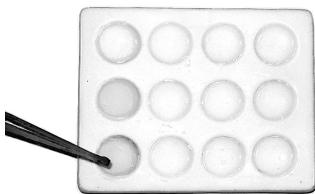


Fig. 14

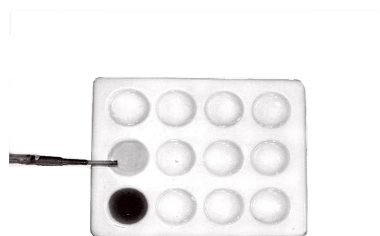


Fig. 15

- 7) Repeat steps 1-6 using 1M sodium hydroxide instead of distilled water. **WARNING:** Sodium hydroxide solution is caustic. Flush with water if it comes in contact with your skin.
- 8) For comparison, repeat steps 4-6 using fresh samples of distilled water and sodium hydroxide that have not been exposed to the gas. These will serve as your control
- 9) Soak all syringes in sodium hydroxide solution (according to the safety instructions at the start of this lab exercise). Organize your data into the following table:

Colorimetric Evaluation of Aqueous Sulfur Dioxide

Treatment	pH (color)	KMnO ₄ (color)
Water + SO ₂		
NaOH solution + SO ₂		
Pure water (control)		
Pure NaOH solution (control)		

Procedure D-1: Gas Absorption by Scrubber Media

- 1) Put on your goggles. Prepare a 60-mL syringe by connecting 2-3 inches of aquarium tubing to the nozzle. Add approximately 1 gram of sodium hydroxide to the syringe, tilting it so that the granules do not pour out through the nozzle. **WARNING:** Solid sodium hydroxide is very caustic. Flush with water if it comes in contact with your skin.
- 2) Add 30 drops of distilled water to the solid, keeping the syringe tilted so that the solution does not pour out (Fig. 16). The dissolution of sodium hydroxide is an exothermic reaction. Allow time for it to cool before going to the next step.
- 3) Once the mixture has cooled down and more than half the solid is dissolved, *carefully* insert the plunger so that there is only 2-4 mL of space for the slurry (Fig. 17). **WARNING:** It is common for the plunger to slip during this step and squirt out its contents. Make sure you are not pointing it towards your lab partner's face! Note down the volume, then go the fume hood.
- 4) Hold upright a capped syringe containing 55-65 mL so that the heavier-than-air sulfur dioxide does not pour out. Note the exact volume of gas, then remove the cap and immediately connect it to the syringe with the slurry; then gently transfer all of the gas to the syringe containing your sodium hydroxide slurry (Fig. 18). You may notice that the

plunger will tend to be drawn in as the slurry-media absorbs the gas. This can happen quite fast.



Fig. 16



Fig. 17



Fig. 18

- 5) Label these connected syringes and place them in a safe place where they can be stored overnight.
- 6) Repeat this procedure with the following salts: sodium carbonate, garden limestone, sodium chloride, and sodium sulfate. Some of these salts will dissolve poorly in 30 drops of water. In this case, simply stir the slurry with a glass rod for 1 minute, then proceed to the next step even if the salts are not dissolved.
- 7) The next day, record how much gas was absorbed by each slurry by noting how far the plunger was pulled in (You will probably be subtracting from 55-65 mL). Go on to Procedures D-2 and D-3.

Part D-2- Colorimetric Evaluation of Gas Product

- 1) Put on your goggles. If there is 20 mL or more of gas the next day, transfer this back to the syringe without the slurry (Fig. 19).
- 2) Obtain a clean syringe and transfer this gas once again to this third syringe. This minimizes contamination of your gas with the slurry. Save the syringe with the slurry for Procedure D-3



Fig. 19

- 3) Add 10 mL of distilled water into this last syringe containing the gas following steps 1-3 from Procedure C.
- 4) Test the gas-saturated water for the presence of aqueous sulfur dioxide by applying steps 4-6 from Procedure C. Organize your data from Procedure D into the following table:

Volumetric and Colorimetric Evaluation of Gas Product

Scrubber reactant	NaOH	Na ₂ CO ₃	Lime	NaCl	Na ₂ SO ₄
Gas volume absorbed (mL)					
pH (color)					

based on exposure of water to the gas					
KMnO ₄ (color)					
based on exposure of water to the gas					

Part D-3: Colorimetric Evaluation of Solid Product

- Put on your goggles. Scrape out as much of the slurry as possible from the syringe and place it in a labeled 50-mL beaker (Fig. 20). *You may add some drops of distilled water to help get out most of the slurry.* Place the beaker in a drying oven (set at about 150 °F) until it is completely dry (1-3 days). **WARNING:** *Solid sodium hydroxide is very caustic. Flush thoroughly with water if it comes in contact with your skin.*
- After it is dry, add 10 mL distilled water to the beaker and stir with a glass rod until the slurry is completely dissolved (Fig. 21). Finally, test the solution for the presence of sulfites (aqueous sulfur dioxide) by applying steps 4-6 from Procedure C. For comparison, prepare fresh samples that have not been exposed to the gas (1g/mL) and apply the same test.



Fig. 20



Fig. 21

- Pour all samples down the drain and run the water for about a minute. Thoroughly rinse all glassware and syringes. Organize your data into the following table:

Colorimetric Evaluation of Solid Product

Scrubber reactant		NaOH	Na ₂ CO ₃	Lime	NaCl	Na ₂ SO ₄
pH (color) reading of dissolved solid	Not exposed to gas (control)					
	Exposed to gas					
KMnO ₄ (color) reading of dissolved solid	Not exposed to gas (control)					
	Exposed to gas					

Procedure E: Oxidation of Aqueous Sulfur Dioxide

WARNING: *Aqueous sulfur dioxide is both corrosive and toxic. Be sure to flush with water for one minute if it comes in contact with your skin.*

- Prepare at least 60 mL of sulfur dioxide-saturated water (see Procedure C). To save time, fill each syringe with 30 mL instead of 10 mL of distilled water (two syringes).

- 2) Place all of the gas-saturated water into a small beaker and add 3 drops of 0.1M iron (III) nitrate to the water. Mix thoroughly with a stirring rod. The iron III ion serves as a catalyst to speed up the oxidation of the bisulfite ions (I).
- 3) Test the gas-saturated water using pH indicator and potassium permanganate (see procedure C). This will serve as your day 0 reading.
- 4) Draw up equal amounts of your gas-saturated water into three 60-mL syringes (about 20 mL each).
- 5) Transfer about 30 mL of oxygen to one of your syringes (using an oxygen-filled syringe prepared by your instructor) and cap the syringe. Repeat this procedure for the second and third syringes using a similar amount of air instead of oxygen. All of your syringes should now have a total volume of about 50 mL (20 mL solution + 30 mL gas).
- 6) Press down the plunger of each capped syringe and shake it for at least 20 seconds to make sure that the water is saturated with this new gas.
- 7) Label each syringe and store overnight horizontally to further enhance gas absorption.
- 8) The next day (day 1), test only with potassium permanganate. *The contents may be under pressure. Before taking the sample, hold the syringe upright and remove the cap. This will serve to equalize the gas pressure in the syringe so that the pressure does not push out all the contents of your syringe during sampling.*
- 9) After sampling, replace the cap on the syringe with oxygen, then press down the plunger and shake for 20 seconds. Do the same after sampling from one of the syringes with air.
- 10) You need to exchange all of the air in the third syringe with air. You can do this by holding the syringe upright and expelling all of the air then pulling back the plunger to refill with the same amount of air. **WARNING:** *It is common for the plunger to slip forward and squirt out some of the corrosive solution, so be sure to point the syringe away from your partner's face! If the plunger is stuck before you begin, carefully loosen it by forcing it backwards, then gently pushing it forward. Forcing the plunger forward may cause it to jerk and release the caustic solution into the surroundings.* Replace the cap then press down the plunger and shake for 20 seconds.
- 11) Leave overnight. Repeat steps 8-10 for days 2-7 (or until the materials in at least two of the syringes no longer react with the permanganate).
- 12) On the last day of testing, test, using both pH indicator and potassium permanganate.
- 13) Discard the solutions down the drain and soak all syringes in sodium hydroxide solution (according to the safety instructions at the start of the lab). Organize your data into the following table:

Effectiveness of Different Strategies for Oxidizing of Aqueous Sulfur Dioxide

Treatment		O ₂	Air (w/exchange)	Air(no exchange)
pH (color)	Day 0			
	Final			
KMnO ₄ (color)	Day 0			
	Day 1			
	Day 2			
	Day 3			
	Day 4			
	Day 5			

Literature Cited:

1. Tsunogai, S. 1971. *Oxidation of sulfite in water and its bearing on the origin of sulfate in meteoric precipitation*. *Geochemical Journal* 1971, 5, 175-185.

Questions (A-C):

1. How did exposure to sulfur dioxide affect the pH of distilled water? What reaction was involved?
2. How did exposure to sulfur dioxide affect the reaction of the distilled water with potassium permanganate? What reaction was involved?
3. Did the addition of sulfur dioxide affect the pH of the sodium hydroxide solution? Why or why not?
4. How did exposure to sulfur dioxide affect the reaction of sodium hydroxide solution with potassium permanganate? What reaction was involved?

Questions (D):

5. Which solids (slurries) reacted with the sulfur dioxide? How do you know?
6. Which syringe absorbed the most gas?
7. Does little or no change in the amount of gas necessarily indicate that the slurry did not react with the sulfur dioxide? Explain:
8. If a reaction took place without a net loss of gas, how did you know? What reaction was involved?

Questions (E):

9. Which treatment was most effective for sulfite oxidation? Why?
10. Which treatment was least effective for sulfite oxidation? Why?
11. Does sulfite oxidation affect pH? Why or why not?
12. During the manufacture of flue gas desulfurization gypsum, why is it important to convert all of the sulfites into sulfates? What might be the problem with drywall that contains significant amounts of calcium sulfite?