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"Geber's Method" and "Greener" Synthesis of Sulfuric Acid

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Abstract

The release of sulfur dioxide (SO_2) into the atmosphere as a result of man's domestic and industrial activities is a great environmental concern. A significant source of SO_2 release into the atmosphere is industrial manufacture of sulfuric acid. A synthetic procedure that is linked with the medieval alchemist named Geber is introduced as a method to be considered for "greener" synthesis of sulfuric acid. The method is based on the calcination of "green vitriol" in the presence of air. The synthetic pathway leads to the production of sulfuric acid without producing SO_2 and is also environmentally advantageous as its starting material is a green natural product ("green vitriol") and as it leaves no environmentally unfriendly byproduct.

Key words: atmosphere; Geber; green vitriol; sulfur dioxide; sulfur trioxide; sulfuric acid

Introduction

Sulfur dioxide (SO_2) is released into the atmosphere as a result of domestic and industrial activities. When SO_2 is released in the heart of densely populated areas, it does great damage to the respiratory organs of man and animals and most importantly it is one of the precursors of acid rain. Acid rain does great damage to buildings, and perhaps most seriously to plants, lake-waters, and aquatic life [1]. Sulfuric acid (H_2SO_4) is the most commonly known acid in the world of chemistry, and the *contact process* for the production of sulfuric acid is one of the most important processes in the inorganic chemical industry [2]. In the contact process sulfuric acid is produced through the reaction of sulfur trioxide (SO_3) and water (in 98% H_2SO_4) [1]. However, the contact process is based on the catalytic oxidation of SO_2 to SO_3 in the presence of vanadium (V) oxide [2]. The oxidation of SO_2 to SO_3 is a reversible reaction, and large quantities of unconverted SO_2 are vented to the atmosphere each year [1]. Therefore, as measures to minimize the release of SO_2 into the atmosphere are necessary, introducing methods for the synthesis of sulfuric acid that eliminate or minimize the venting of SO_2 to the atmosphere is to be considered.

Calcination, which refers to heating an inorganic material to a high temperature without fusing in order to drive off volatile matter or to effect a chemical change, dates back to medieval era and is still common in modern-era chemistry. However, the word "calcination" is linguistically related to the Arabic word "*al-taklis*". *Ibn-Sina* (Latin Avicenna, 980-1037) [3], who is a medieval physician and philosopher, in his book on alchemy titled *Risalat al-kimiya'* (The Treatise of Alchemy) [4] lists and describes calcination as well as other chemical processes, such as combination, sublimation, and solvation. Before *ibn-Sina*, however, calcination was described scientifically by the father of Arabic alchemy, Geber (*Jabir ibn-Hayyan*), who flourished in al-Kufah about 776 [3]. Geber's doctrines and experiences have been appropriated by his disciples [5], and his name (that is the European version of the Arabic name *Jabir*) appears in medieval Western literature in the 13th and 14th centuries in the collections of alchemical works in the Latin language. Many discoveries in chemistry, including that of nitric acid (HNO_3) and ammonium chloride (NH_4Cl), are said to be Geber's [6], and the discovery of sulfuric acid is often linked with him [7]. This paper introduces "Geber's method" of producing sulfuric acid through the calcination of "green vitriol" as a synthetic procedure to be considered for "greener" production of sulfuric acid and demonstrates that "Geber's method" of producing sulfuric acid is not only of significant historical value, but also environmentally valuable due to having the potential to minimize the annual global emission of SO_2 from sulfuric acid processing plants.

Experimental Details

Although modern historiography has argued that the author is a person it calls Pseudo-Geber and not *Jabir ibn-Hayyan*, a passage from a part of a Latin work under the name Geber in the late Middle Ages has been considered to be the earliest known recipe for sulfuric acid [7]. In a recent translation this passage reads [7]: *"Luna is also yellowed similarly with a solution of mars. The method of that yellowing which is perfected by vitriol or copperas is as follows. A specific quantity of either of them should be taken, and the part of that which allows itself to be sublimed should be sublimed until it is sublimed with a total expression of fire. After this, what was sublimed should be sublimed again with a suitable fire, so that it be gradually fixed, until the greater part of it is fixed. Then let it be calcined carefully with intension of the fire, so that a greater fire can be administered to it for its perfection. Then it should be dissolved into red water to which there is no equal."* It is understood that in a series of alchemical experiments Geber calcined "green vitriol" [8] (that he had most probably obtained from the copper deposits of Rio Tinto, Spain, considering the places of its abundance). He might have expected a gaseous stream if, as the narratives state [8], following the calcination reaction he introduced a gaseous stream into water.

Results and Discussion and Conclusion

Today we understand some of the steps of what Geber experienced as a multi-stage process. "Green vitriol" (hydrated iron(II) sulfate: $FeSO_4.7H_2O$) is available in nature as a green, sweetish mineral [9]. The first chemical change that occurs when "green vitriol" is heated is the loss of its hydration water as a vapor.

$$FeSO_4.7H_2O\ (s) \rightarrow FeSO_4\ (s) + 7\ H_2O\ (g) \qquad (1)$$

It is extremely unlikely for an alchemist of the 8th-and-9th-centuries period to have had a compound thermally decomposed in any inert atmosphere. Therefore, assuming that the heating process was continued in air, studying thermal decomposition of iron(II) sulfates by Gallagher and co-workers [10] shows that the next chemical reaction was according to the following equation:

$$4\ FeSO_4\ (s) + O_2\ (g) \rightarrow 2\ Fe_2O(SO_4)_2\ (s) \qquad (2)$$

As equation (2) involves the production of no gas, the heating process must have continued in order to produce a stream of SO_3 gas needed to produce sulfuric acid. Indeed, Gallagher et al.'s study [10] shows that if heating continues, the solid product of equation (2) will decompose to iron(III) oxide and SO_3 gas as follows:

$$Fe_2O(SO_4)_2\ (s) \rightarrow Fe_2O_3\ (s) + 2\ SO_3\ (g) \qquad (3)$$

Finally, when the produced SO_3 (g) stream enters water, sulfuric acid will be the product:

$$SO_3\ (g) + H_2O\ (l) \rightarrow H_2SO_4\ (aq) \qquad (4)$$

Accepting that Geber had an alert observation, we can state that following the synthesis he observed every characteristic of the product that he, being an alchemist of the 8th-and-9th-centuries period, was able to observe and then "identified" the product, what we often call sulfuric acid.

The starting material in "Geber's method" ("green vitriol") is both an environmentally friendly compound and available in nature as a mineral [9]. In industrial manufacture of H_2SO_4, about 40% of the SO_2 comes from the roasting of sulfide minerals and about 60% of the SO_2 comes from the burning of sulfur [1]. "Geber's method" is environmentally advantageous relative to existing industrial manufacture of H_2SO_4 in which SO_2 comes from the roasting of sulfide minerals notably iron pyrite, or ores of Cu, Ni, and Zn during the production of these metals [1]. Although both methods involve formation of byproducts, Geber's synthetic pathway does not vent any SO_2 to the atmosphere. "Geber's method" is also environmentally advantageous relative to existing industrial manufacture of H_2SO_4 in which SO_2 comes from the burning of sulfur. Although that existing process does not involve formation of any byproduct, the oxidation of SO_2 to SO_3 is reversible and the reverse reaction leads to the production of SO_2 [1], which leads to SO_2 being vented to the atmosphere [1]. Geber's synthetic pathway does not vent any SO_2 to the atmosphere. Also, although "Geber's method" does leave a byproduct (iron(III) oxide), the byproduct is not only green but also can be smelted with carbon to produce iron according to the following overall reaction [2]:

$$2\ Fe_2O_3\ (s) + 3\ C\ (s) \rightarrow 4\ Fe\ (l) + 3\ CO_2\ (g) \qquad (5)$$

In conclusion, it is important to note that "Geber's method" does not vent any SO_2 to the atmosphere if Geber's synthetic pathway is followed exactly. Therefore, in order to have "Geber's method" considered for "greener" industrial scale manufacture of sulfuric acid, it is necessary to minimize the decomposition of the SO_3 produced in equation (3) to SO_2 and O_2. That can be achieved by allowing the SO_3 produced in equation (3) to react with water (in 98% H_2SO_4) as soon as possible after the SO_3 is produced. Also, any excess stream of SO_3 should be directed back to the reaction chamber via a feedback loop. Further, it is noteworthy that the method referred to as

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"Geber's method" being advocated in this paper is not intended to substitute the *contact process*. It is rather to supplement it so that the annual global emission of SO_2 from sulfuric acid processing plants is minimized.

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