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Environmental problem from the Combustion of Sulfur in Mishraq Field

Wedad H. Al-Dahhan[1], Ali Abd Ali[1]Emad Yousif[1]*
[1]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
*Corresponding author E-mail: emad_yousif @hotmail.com

Abstract: Al-Mishraq sulfur mine (25 miles to the north of Qayyarah in Mosul province, Iraq) has been considered as the largest sulfur mine in the world. The site has caused two catastrophic events in 2003 and 2016 due to combustion of elemental. sulfur. The release of about 600 k tons of sulfur dioxide. (SO_2) led to the formation. of the largest. non-volcanic. sulfur cloud ever measured by satellites. Gaseous. sulfur dioxide is. readily. soluble. in water, and reacts with water molecules in the. atmosphere. to produce. sulfuric acid rain which can cause serious damage to environment. We report here the adverse effects upon sulfur dioxide evolution as result of sulfur combustion as. well. as. acid rain. We also highlight some major health problems that people. have. suffered. so far from sulfur dioxide evolution.

Keywords: Sulfur, Sulfur dioxide, Mishraq, Acid rain

INTRODUCTION

Sulfur is a yellowish crystalline solid which is highly reactive towards all elements except gold, platinum iridium , tellurium , and the noble gases; nonetheless, sometimes exist in neat, native form. Sulfur usually occurs as sulfide and sulfate minerals (Greenwood, N. et al., 1997).Basically, elemental sulfur is originated in the vicinity of hot springs and volcanic areas around the world (Rickwood, P. 1981).

Mishraq sulfur state company is one of Iraqi Ministry of Industry and Minerals companies. It was established in 1969, and the sulfur production started late 1971 (website 1). Mishraq Sulfur mine has around 320 million ton sulfur (Carn, S. et al., 2004).

Sulfur burns with a blue flame with formation of sulfur dioxide (Figure 1), which has a suffocating and irritating odor. Sulfur is insoluble in water, but soluble in carbon disulfide and, to a lesser extent, in organic solvents, such as benzene and toluene (Wiberg, E. et al., 2001).

Figure 1: When burned, sulfur melts to a blood-red liquid and produces a blue flame that is clearly noticed in the dark (Wiberg, E. et al., 2001).

As part of our own interest in the field in safety and security (Ali, A. et al., 2017 ; Ali, A. et al., 2016 ; Al-Zuhairi, A. et al., 2016 ; Yousif, E. et al., 2016; Ali, A. et al,2017 ; Rasool, R. et al., 2016; Al-Dahhan, W. et al., 2016 ; Hussein, F. et al., 2017 ; Ibrahim, A. et al., 2016; Yousif, E. et al., 2017), we have improved many ideas and aspects.

Sulfur is only slightly flammable at normal conditions in pure oxygen. However, it burns with a very nice blue flame. The products of the combustion are sulfur dioxide and sulfur trioxide as illustrated in the following chemical equations:

$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$

$2S_{(s)} + 3O_{2\,(g)} \longrightarrow 2SO_{3\,(g)}$

These substances react with water in the air to produce sulfurous and sulfuric acid, respectively (Emsley, J. 1998). Sulfur dioxide (SO_2) is a colorless, non-combustible, toxic gas. The most important physical characteristics are summarized in Table 1. Since the critical temperature is very high, sulfur dioxide can easily be condensed by compression to give a colorless, readily mobile liquid (Hasenberg, L.2008).

Table 1: Physical characteristics of sulfur dioxide (Hasenberg, L.2008).

Properties	Value
Melting point (101.3 kPa)	(–75.65 °C)
Density at 263 K (–10 °C)	1.46 g/cm^3
Boiling point under 101.3 kPa	(–10 °C)
Normal density at (0 °C) (101.3 kPa)	2.93 kg/m^3
Relative density based on air = 1 (0 °C), 101.3 kPa)	2.263
Critical temperature	(157.35 °C)

Gaseous sulfur dioxide is readily soluble in water. Its solubility increases as the partial pressure increases and the temperature drops. Figure 2 shows this relationship.

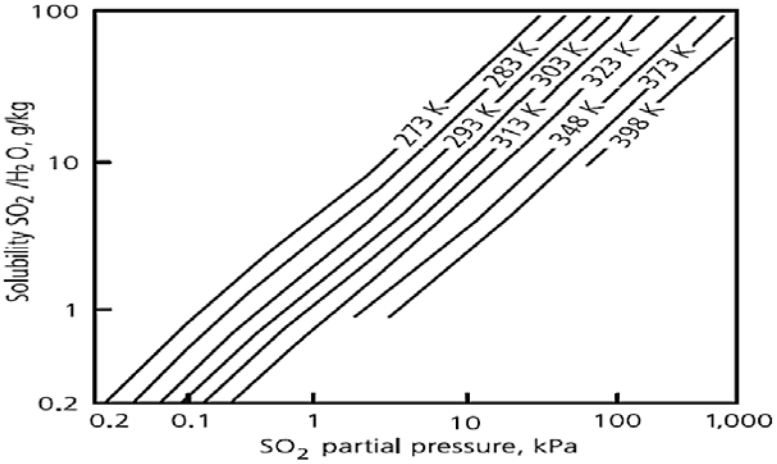
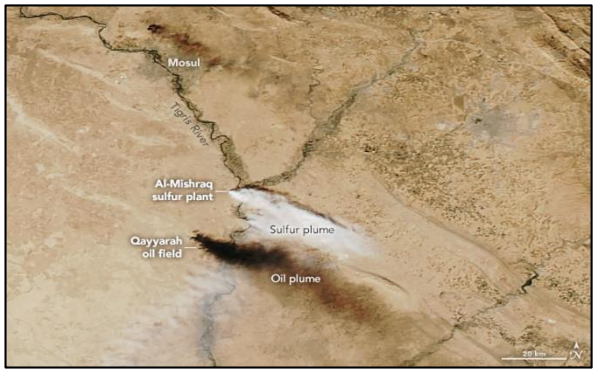


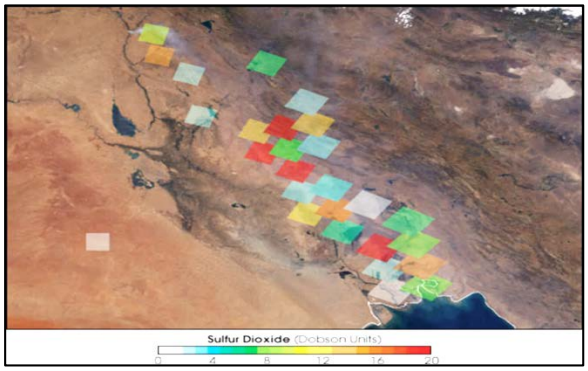
Figure 2: Solubility of sulfur dioxide in water as a function of the temperature and SO_2 partial pressure (Hasenberg, L.2008).

2- Literature review

A fire started at the Al-Mishraq municipal Sulfur plant near Mosul, Iraq on 24th of June 2003 and burned for almost a month. Combustion of elemental sulfur produced dense clouds of sulfur dioxide (SO_2) that were detected from space by the Earth Probe Total Ozone Mapping Spectrometer (EP TOMS) as depicted in Figure 3 (website 2). This event is the largest non-volcanic SO_2 emission detected to date by any TOMS instrument. The TOMS instrument has been measuring volcanic sulfur dioxide SO_2 clouds from space since 1982 (Carn, S. et al., 2004).



Picture 1



Picture 2

Figure 3 (Picture 1&2): Combustion of elemental sulfur in the fire produced dense clouds of sulfur dioxide (SO_2) that were detected from space by the Earth Probe Total Ozone Mapping Spectrometer (EP TOMS) (website 2).

In early 2003, 20,000 U.S soldiers from the 101st Airborne from Ft. Campbell, KY were positioned to northern Iraq as part of military operations of the US-Coalition forces. In June 2003, opposing forces set fire to the Mishraq Sulfur Mine. Airfield West (Camp Q West), a major military supply airstrip and the primary area of positioning for the 101st Airborne .

At that time, the Mishraq Sulfur Mine was burned for more than four weeks and caused the release of 19000 ton of SO_2 a day. This represents the largest man-made release of SO_2 on record. Satellite imaging recognized that the SO_2 cloud extended in a Southeast direction over the city of Mosul and Camp Q West.

With regards to the severe effects of SO_2 on health, SO_2 gas causes a hard lung injury at very low concentrations (0.1 ppm). The U.S soldiers were exposed to levels of five hundred times higher than this. The residents of this area including soldiers suffered from serious skin, and eye irritation with notable breathing problems.

Over 80 soldiers from the area were examined, and it was found that 34 of them were suffering from constrictive bronchiolitis, sarcoidosis, respiratory bronchiolitis, and respiratory bronchiolitis with interstitial lung disease or hypersensitivity pneumonitis. Many of these conditions are irreversible and untreatable (Robert, F. et al., 2004).

3- IS burned sulfur stocks near Mosul, creating hazard for troops, and locals

In 21st of October 2016, so-called Islamic State (IS) set fire to sulfur stocks at a factory south of Mosul (Figure 4), creating a huge cloud of toxic smoke. A cloud of white smoke covered the area around the Mishraq sulphur plant, circulating with black fumes from oil wells as shown in Figure 5.

Figure 4: Fire in sulfur south of Mosul

Figure 5: A cloud of noxious smoke

Around a thousand people in the area affected by the smoke causes severe burns to eyes and hurt to their noses and throats. Even the exposure to high concentration of SO_2 for a short period of time can be life threatening, and children might be susceptible to its toxic effect as they breathe more air for their body weight than adults as seen in Figure 6. Furthermore, people who suffer from asthma or similar conditions might be at higher risk if they inhaled that smoke. Another important effect worth mentioning is that the toxicity of sulfur dioxide is estimated about 700 times that of carbon dioxide.

Picture 1

Picture 2

Figure 6 (Picture 1&2): People in Mishraq affected by the smoke causes difficult to breathe

4- Environmental effects of SO_2 and other sulfur oxides

Sulfur dioxide can cause serious effects on our environment. It is absorbed by soils and plants, affecting badly on our ecosystem, and it can even be captured within and below clouds, which increases the chance of acid rain (website 3).

It can be detected by taste and smell in the range of 1,000 to 3,000 micrograms per cubic meter. At concentrations of 10,000 µg/m^3, it has a pungent , unpleasant odor. Sulfur dioxide dissolves readily in water present in the atmosphere to form sulfurous acid (H_2SO_3). About (30%) of the sulfur dioxide in the atmosphere is converted to sulfate aerosol (acid aerosol) (USEPA (United States Environmental Protection Agency), 1998). Sulfur aerosols impact human health, ecosystems, agriculture, and global and regional climate (Smith, S. ,2011)

Sulfur trioxide (SO_3), another oxide of sulfur, is either released directly into the atmosphere or produced from sulfur dioxide and is rapidly converted to sulfuric acid (H_2SO_4) (USEPA (United States Environmental Protection Agency), 1998)

Even minor quantities of sulfur dioxide can damage plants and trees and reduce their growth. At high concentrations, gaseous SOx can destruct trees and plants by damaging foliage and decreasing growth (website 4).

Sulfur oxide emissions cause adverse impacts to flora, including forests and agricultural crops. Extensive studies in the United States and elsewhere have shown that plants exposed to high ambient concentrations of sulfur dioxide may lose their foliage, become less productive , or die early (website 4). Some species are even more sensitive to exposure than others. Plants in the close vicinity of emission sources are more at risk.

4.1 Acid Rain

Formation of sulfuric acid by radical chemistry
In the gas phase, sulfur dioxide is oxidized by reaction with the hydroxyl radical via an intermolecular reaction :

$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$

This is followed by:

$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3$

In the presence of water, sulfur trioxide (SO_3) is converted rapidly to sulfuric acid:

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

Figure 7 shows the effect of sulfur dioxide on plants.

Picture 1

Picture 2

Figure 8 (pic.1 &2): Effect of acid rain on plants

4.2 Materials

Sulfur dioxide emissions may affect building stone and ferrous and nonferrous metals. Sulfurous acid, formed from the reaction of sulfur dioxide with moisture, boosts up the corrosion of iron, steel, and zinc. Sulfur oxides react with copper to produce the green coating of copper sulfate on the surface of the copper. Acids in the form of gases, aerosols, or precipitation may chemically erode building materials such as marble, limestone, and dolomite. Of particular concern is the chemical erosion of historical monuments and works of art. Sulfurous and sulfuric acids formed from sulfur dioxide and sulfur trioxide when they react with moisture may also damage paper and leather (Nicholas P. 2001)

4.3 Water

Both the lower pH and higher aluminum concentrations in surface water that occur as a result of acid rain can cause damage to fish and other aquatic animals. At pH lower than 5, most fish eggs will not hatch and lower pHs can kill adult fish (website 5), see figure 9.

Figure 9: Acid rain cause damage to fish

4.4 Soil

Soil can be seriously damaged by acid rain. Some tropical microbes can quickly consume acids but other microbes are unable to survive at low pH, as enzymes of these microbes are dysfunctional by the acid. Aluminum exists in soils in a various forms and bound to the soil constituents, particularly clay particles and organic matter. When soil pH drops, aluminum becomes soluble and the amount of aluminum in the soil solution increases as depicted in Figure 8.

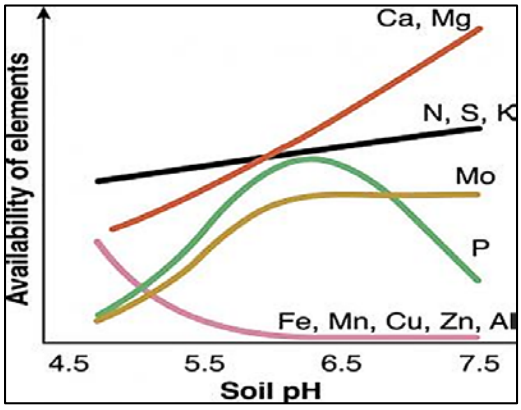


Figure 8: A representation of the relationship between soil pHCa and nutrient availability. In acidic soils, some nutrients may be insufficiently available for optimal plant growth and aluminum may become toxic (website 6).

As a rule of thumb, soil aluminum concentration of 2-5 ppm is toxic to the roots of sensitive plant species and greater than 5 ppm is toxic to tolerant species (website 6). Figure 9 illustrates the effect of acidic soil on barley seedlings grown.

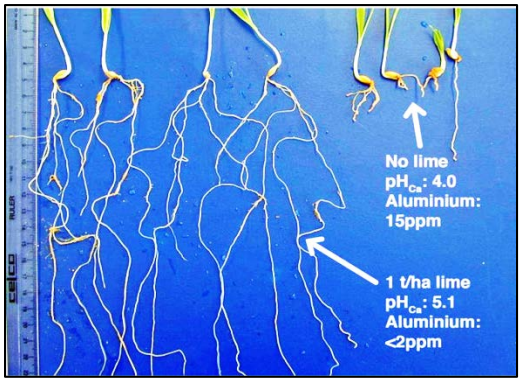


Figure 9: Barley seedlings grown in limed (left) and unlimed (right) acidic subsurface soil; there are no symptoms of aluminum toxicity in the limed treatment (website 6)

5- Conclusion

Sulfur dioxide emissions can affect people in the area affected by the smoke causes severe burns to eyes and hurt to their noses and throats. Even the exposure to high concentration of SO_2 for a short period of time can be life threatening, and children might be susceptible to its toxic effect as they breathe more air for their body weight than adults. Sulfur dioxide can cause serious effects on our environment. It is absorbed by soils and plants , affecting badly on our ecosystem, and it can even be captured within and below clouds, which increases the chance of acid rain. Sulfur dioxide emissions may also affect building stone and ferrous and nonferrous metals.

6-Acknowledgements

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