

Importance of Chemical Reactivity in Understanding Environmental Hazard

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ABSTRACT

The focus of the 'Chemistry of Hazardous Materials' course offered during the 1995 fall semester is upon 'chemical reactivity' and its relationship to environmental hazard. The Resource Conservation and Recovery Act (RCRA) defines a hazardous substance as that which exhibits the characteristics of chemical reactivity, corrosivity, ignitability, and toxicity. There are other definitions of hazardous materials that use characteristics that are not listed in the RCRA definition. Absent chemical reactivity there would be no hazardous characteristics such as corrosivity, ignitability, or toxicity exhibited by a substance. There are certain phenomena and factors that are important within the context of environmental hazard, because they promote chemical reactivity. These phenomena and factors include, but are not limited to, type of substance and position in the periodic table if substance is an element, state (whether solid, powdered solid, liquid, or gaseous), buoyancy effects, heat and mass transport effects, pressure, temperature, wind velocities, weather conditions, catalysis, compatibility of chemicals during storage or transport. This paper presents the concepts of chemical reactivity, influencing factors, and their role in creating environmental hazard. The three instructors: a Ph.D. chemist, a master degree chemical engineer with thirty five (35) years industrial experience, and a Ph.D. chemical engineer with 5 years industrial experience used projects, case studies, video taped demonstrations as examples to illustrate the crucial role chemical reactivity plays.

Introduction

I was part of a team of three instructors, who taught a course titled 'Chemistry of Hazardous Materials' which was offered under the hazardous waste management program. My students were employees in local industry and most had little or no background in chemistry. It is important to teach these students that reactivity is responsible for most hazards. The motivation for this paper stems from the thorough conviction that chemical reactivity together with influencing factors serve as the basis for a substance to be considered a potential hazard. Hazard is defined as a chemical or physical condition that has the potential for causing damage to people, property, or the environment [1]. The nature and state of a substance have a direct bearing on its reactivity. Other factors that promote chemical reactivity include, buoyancy effects, heat and mass transport, wind velocity, weather condition, pressure, temperature, catalysis, and chemical compatibility during storage and transportation. These will be discussed in relation to their contribution toward the potential environmental hazard.

Nature of substances and influencing factors

- I. Certain elements in group I or in groups V through VII of the periodic table exhibit reactive and hazardous nature. The periodic table determines both the reactivity of these elements as well as the hazardous nature of some of the heavy metals such as cadmium, lead, and mercury. For example, mercury is more dangerous in ionic form especially as organic mercury. Mercury vapor can lead to adverse biological effects by causing tremor and psychopathological symptoms when it penetrates the brain through the bloodstream.

Some compound forms of nitrogen and oxygen are likewise hazardous. For example, most explosives are compounds of these two elements. The eight oxidation states of nitrogen allow for transition from one state to another with energy release. Each transition indicates a reaction. Most compounds of nitrogen and oxygen are by nature, very reactive or unstable. Examples of these compounds include sodium azide, ammonia, and nitrocellulose. Similarly, oxygen-containing compounds of nitrogen can provide the oxygen needed to initiate combustion reactions. Examples are trinitrotoluene, nitrocellulose, ammonium nitrate. Compounds containing nitrosamine groups ($-\text{N}-\text{N}=\text{O}$) are carcinogenic. Some compounds containing group VII elements, such as CFCs and dioxin constitute environmental hazard. Dioxin, a chlorinated organic compound is one of the most toxic substances known to man. Phosphene, a highly toxic and flammable gas contains a group V element, phosphorus, which can exist in three oxidation states.

Notice that oxidation state plays an important role in the reactivity of the substances. Ozone, which consists of three atoms of a group VI element, oxygen, generates reactive free radicals in lipid peroxidation – a manifestation of tissue damage.

- II. Explosives are unstable substances or a mixture of substances which when exposed to a suitable energy activator undergoes a rapid and violent decomposition reaction releasing large volumes of burning gas and heat energy. The explosion is termed detonation or deflagration depending on whether the burning gas forms pressure wave front that is travelling faster or slower than the speed of sound.

The transport of heat through the burning gas by conduction, convection and radiation coupled with the shattering impact from the ensuing shock waves helps sustain the reaction. Pressure effects in an explosion can propagate adverse reaction in this type of hazardous chemicals, because the resulting shock waves act as energy activator. The shock waves activate unreacted portions of the explosive causing it to explode. List of explosives include oxidizers, organic peroxides, gun powder, dynamite, nitroglycerin, trinitrotoluene, nitrocellulose, picric acid, mercury (II) cyanate, and pentaerythritol tetranitrate—most of which contain nitro group, $-\text{NO}_2$.

- III. Incompatible chemicals are those that react when in contact with each other. A list of such chemicals includes water reactive materials which liberate toxic gas and heat. If the gas is flammable, the heat becomes more intense. Examples of these are mixtures of powdered pyrophoric metals and water which produce flammable and explosive

hydrogen. Such metals include magnesium, zirconium, titanium, aluminum, and zinc. The powder forms of these metals increase the surface area of reaction thereby enhancing the exothermic reaction. Combining water with some organo-metallic compounds such as trimethyl aluminum or dimethyl cadmium produces explosive mixture. Other incompatible mixtures include hypergolic reactive materials which contain oxidizers and chemical activators. This combination releases oxygen and flammable vapors. The chemical activator, which may be a metal, non-metal, or non-salt, has great affinity to liberate the oxygen in the oxidizer. Methanol and hydrogen peroxide is an example of a hypergolic mixture in which methanol is playing the role of a chemical activator.

- IV. Temperature and heat effects aid chemical reactivity of hazardous substances as previously mentioned. The heat may help sustain the reaction. In addition, Arrhenius temperature dependent specific rate constant, k , given by $k = k_0 \exp(-E/RT)$ predicts increased reaction rate with rising temperature. The variables k_0 , E , R , and T are pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively.
- V. Catalysis effect promotes the adverse reaction of the hazardous substances by decreasing the activation energy. Also, Arrhenius equation predicts increased reaction rate with decreasing activation energy.
- VI. Wind velocity and substance volatility promote mass transport by conveying the substance to a site where adverse reaction occurs. For examples, toxic fumes carried by the wind can lead to acid fog. Rain can react with toxic gases such as NO_x , CO , H_2S , SO_2 , and HCl (gas) to form acid rain, which when transported can lead to detrimental effects on animals, plants and structures. Damage to aquatic life, reduction in forest and crop productivity, leaching of nutrient cations and heavy metals from soil and rock, dissolution of metals such as lead and copper from water distribution pipes, corrosion of exposed metals, and dissolution of exposed surfaces of limestone buildings and monuments can be the direct result of acid rain.
- VII. Buoyancy effect acts as a type of mass transport mechanism. For example, extinguishing burning oil fire with water does not work, because the lighter oil floats on the water and continues to combust.

Conclusion

The author concludes that without chemical reactivity, there would be no hazardous characteristics such as toxicity, ignitability, corrosivity, or flammability exhibited by a substance. Chemical reactivity enhances the hazardous nature of a substance. Some factors directly promote chemical reactivity, while others help convey hazardous substances to sites where adverse chemical reaction takes place. Understanding the role of chemical reactivity and influencing factors can help alert students to the fact that chemical reactivity is a basic criteria in selecting environmentally friendly alternatives to replace hazardous materials. Several authors, McCright and Bermiller (2), and Dorland and Baria (3) agree that any negative impact on the environment must be minimized as the twentieth century draws to a close and the new millenium

ushers in. The author affirms the need to understand the causes of the negative environmental impact. Chemical reactivity can shed some light on the understanding of these causes. Though the treatment above is qualitative rather than quantitative, it illustrates that most substances would not be hazardous as we know it, if it were possible to suppress chemical reactivity. The author admits that the list of substances and factors examined are by no means exhaustive.

References

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Dr. Charles U. Okonkwo graduated with bachelors and master’s degrees in chemical engineering from Iowa State University, and a Ph.D. in chemical engineering from the University of Florida. He has worked as senior process engineers for both the chemical and semiconductor industries. Since joining the College of Technology and Applied Sciences as a lecturer, he has taught graduate courses in hazardous waste management program, and undergraduate and graduate courses including thermodynamics, fluid dynamics, statistical process control and design of experiments in the Department of Manufacturing and Aerospace Engineering Technology. His emphasis has now changed from waste management to waste minimization and pollution prevention, and design concepts for environmentally safe manufacturing. Prior to joining the college, he taught in the Department of Mathematics at Arizona State University.