

BENEFICIAL AND HAZARDOUS ASPECTS OF CLAYS IN NATURE: A BRIEF OVERVIEW

Of the different types of reactions taking place continuously in the environment, some are activating reactions that contribute to environmental pollution and contaminations. Other reactions that resist environmental pollution or contamination are the neutralising reactions. The clay minerals, being very stable in the condition prevailing at the surface of earth, generally do not participate in activating reactions, though the clay particles from waste dumps may have negative impacts on the air, soil and water sources of surrounding regions. Clay minerals can remove the ions of pollutants and contaminants from solutions. This property enables them to play very important roles in many natural neutralising reactions and facilitate their applications in many pollution control measures.

16.1 INTRODUCTION

Environment is the sum total of all the surroundings of a living organism, and it essentially consists of all the physical, chemical and biotic factors acting upon that organism. The environment in which we live includes other living organisms (different types of plants and animals), inorganic matters (air, water, soil etc.) and natural processes, which provide conditions for our survival, development and growth. The study of the environment is a multidisciplinary approach; and numerous scientists of various disciplines throughout the world are actively engaged in studying the different aspects of the environment, especially the human impacts on its integrity. Consequently the terminologies related to different aspects of the environment vary greatly in the works of

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different authors. The ambiguity thus arising for the definition of the terms environmental pollution, contamination, environmental degradation etc. may be confusing for the students. The definitions of those terms and their brief explanation are therefore presented here.

Environmental pollution: It is the addition of any substance (solid, liquid or gas) or any form of energy (heat, sound etc.) to the environment at a rate faster than it can be dispersed, diluted or decomposed. As a result it gradually accumulates with time and causes damage to the environment when the accumulation crosses a certain limit.

The substance or energy introduced into the environment that has undesired effects is known as a *pollutant*. A pollutant may cause long- or short-term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health or property values.

The three important components of the environment, i.e. the air, water and soil, can be polluted by the anthropogenic activities.

Air pollution is the release into the atmosphere of various gases, finely divided solids, or finely dispersed liquid aerosols at rates that exceed the natural capacity of the environment to dissipate and dilute or absorb them. These substances may reach concentrations in the air that cause undesirable health, economic or aesthetic effects.

Water pollution is the release of substances into surface water bodies or subsurface groundwater to the point where the substances interfere with the beneficial use of the water or with the natural functioning of ecosystems.

Soil pollution is the deposition of solid or liquid materials in the soil in a manner that can decrease the fertility of the soil, destroy the plants or threaten public health.

Environmental contamination: It is the unintended presence or introduction of biological, chemical, physical or radiological substance *which are normally absent in the environment*. These substances, known as *contaminants*, can adversely affect living organisms through air, water, soil, food etc. when present in sufficient concentration.

It is to be noted here that contaminants are not normally present in the environment and generally introduced by anthropogenic activities. But pollutants may be present naturally in the environment in trace amounts, and is harmful only when its concentration in nature crosses a particular limit. For example, carbon monoxide is a contaminant, which is not present in air in normal condition. But carbon dioxide is a pollutant which is naturally present in the air, and has harmful effect on the environment when its concentration crosses a certain limit.

Environmental degradation: It is the deterioration of the environment through change or disturbance in the quality or quantity of natural resources such as air, water and soil which may bring about the destruction of ecosystems, extinction of wildlife and human health hazards. It is a more generalized term

that includes any physical or chemical change in the environment perceived to be harmful or undesirable. Depletion of the freshwater sources and introduction of a harmful chemical in water are both considered as environmental degradation, while only the latter is considered as environmental pollution.

Clays, like most other natural substances, have some beneficial and some hazardous impacts on the environment. As described in Part I, clays have a tendency to adsorb and immobilize ions. This property enables clays to remove ions of pollutants and contaminants from leachates and waste water, thus reducing pollution and contamination. It also facilitates the use of clays in different pollution control measures like carriers of pesticides, liners in waste disposal etc. Clays can also be used in nuclear waste management: clay buffers are built from smectite-rich clays into which the containers of radioactive wastes can be safely disposed (Pusch, 2006).

On the other hand, tendency of the clays to be suspended easily in air (owing to their very fine grainsize), and their property to absorb water and produce plastic mass etc. may cause environmental degradation in certain circumstances.

The harmful effects of clay mining and the uses of clays to resist pollution are described elaborately in the next chapters of Part III. This chapter explains the geochemical processes involved in pollution and contamination, and the roles of clays in those processes.

16.2 ACTIVATING AND NEUTRALIZING REACTIONS AND THEIR CONTROLLING FACTORS

The different types of inorganic and organic waste materials dumped from the mines, factories, construction sites etc. come into contact and react with different natural substances like water (rainwater or surface runoff), atmospheric oxygen, carbon dioxide etc. Some of the reactions are *activating reactions* in which a mineral or an organic material reacts with the natural substances to produce one or more pollutant and/or contaminant. Others are *neutralising reactions* in which one or more reactants (a mineral or organic material or any natural substances) react with the pollutant and/or contaminant produced by activating reactions and transforms them into some non-detrimental form, thus decreasing their quantities in nature and tending to prevent pollution/contamination. Let x be the *net quantity* of a particular pollutant or contaminant X at a certain point of time. It depends on:

- (i) Quantity of X produced in the reaction site by the activating reactions $[x_a]$ and
- (ii) Quantity of X removed from water by the neutralising reactions $[x_v]$

Therefore:

$$x = x_a - x_v \quad (16.1)$$

For example, sphalerite (ZnS), a common mineral present in the waste dumps of sulphide mines, is oxidised by atmospheric oxygen to produce zinc sulphate.



Zinc sulphate, being a highly soluble substance, is a potential pollutant of water and soil. Therefore reaction 17.2 is an activating reaction.

The dissolved ZnSO_4 thus produced reacts with calcite (CaCO_3) to produce smithsonite (ZnCO_3).



Smithsonite is nearly insoluble in water and precipitates from the solution; thus Zn^{++} is removed from water. Nuttal and Younger (2000) found a 22% average reduction in zinc concentration in an open system over a retention time of 14 hours. Therefore reaction 17.3 is a neutralising reaction.

The net quantity of Zn^{++} thus produced is transported and accumulates into the water bodies or soil of surrounding areas; and brings about pollution of water or soil when its proportion crosses a permissible limit.

The activating and neutralising reactions may take place in the waste disposal sites of mines, factories, construction sites etc. The excavated area in the mine may also act as a reaction site, where water percolates and reacts with the minerals of newly exposed rock layers. All these are the *external reaction sites*, from which the pollutants or contaminants are produced and transported to soil or water bodies of surrounding areas, causing pollution or contamination of soil or water respectively. In addition, soil and water bodies themselves become the *internal reaction sites* of activating and neutralising reactions when the unreacted waste materials are transported to them.

16.2.1 Reactions in an Open System and Total Number of Reactable Moles

Let us consider the following hypothetical reaction.



Here a and b moles of the two reactants, A and B respectively, produce c and d moles of the two products C and D respectively. In a close reaction system where no reactant or product can enter from or escape to the surrounding, the reaction will be reversible, i.e. a backward reaction will simultaneously produce A and B from C and D . When accumulation of C and D reaches a certain limit, the rate of forward reaction and backward reaction will be same, and the concentrations of the reactants and products in the system will remain constant unless pressure, temperature etc. changes.

An open reaction system exchanges reactants and/or products with the surrounding. Here the reaction continues until one of the reactants is exhausted. Let X be a reactant having molecular weight M_X , W_X be the amount of X in the

reaction system in gram, and x is the number of molecules of X participating in

the reaction. Then $\frac{W_X}{xM_X}$ determines the following:

- (i) The residual quantity of that reactant X , if any, in the reaction system after the reaction is over.
- (ii) The quantity of products produced in the reaction.

The expression $\frac{W_X}{xM_X}$ is the **Total Number of Reactable Moles** or **TNRM**

of X (Mukhopadhyay and Ghosh, 2010a). In the hypothetical chemical reaction 17.4, if the molecular weights of the four substances are M_A , M_B , M_C and M_D respectively, and W_A gram of A and W_B gram of B are present in the reaction system, then aM_A gram of A reacts with bM_B gram of B to produce cM_C and dM_D grams of C and D respectively.

Then the following situations are possible:

Case I:
$$\frac{W_A}{aM_A} = \frac{W_B}{bM_B} = k \text{ (say)}$$

W_A grams of A will react with W_B grams of B . At the end of the reaction, the residual quantities of both reactants in the reaction system will be zero. kcM_C gram of C and kdM_D gram of D will be produced by the reaction.

Case II:
$$\frac{W_A}{aM_A} < \frac{W_B}{bM_B}$$

W_A grams of A will react with $W_A \frac{bM_B}{aM_A}$ grams of B . The reaction will continue until the entire quantity of A is exhausted in the reaction system.

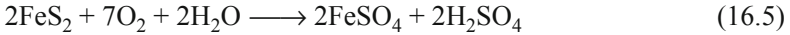
$\left(W_B - W_A \frac{bM_B}{aM_A} \right)$ gram of B will remain unreacted. $W_A \frac{cM_C}{aM_A}$ gram of C and

$W_A \frac{dM_D}{aM_A}$ gram of D will be produced by the reaction.

Similarly, when $\frac{W_B}{bM_B} < \frac{W_A}{aM_A}$, the reaction will continue until the entire quantity of B is exhausted in the reaction system.

So we can infer from the above discussion that *if the TNRM of one of the reactants in the open reaction system is less than that of the other(s), then all of the former will be used up in the reaction and some part of the other(s) will remain unreacted in the system.* Therefore an activation or neutralisation reaction between a mineral and water in an open system will continue until either that mineral or water is exhausted in the reaction system.

Example: Pyrite is one of the most abundant mineral of the sulphide deposits. It may also be present in coal seams or in the shale beds associated to them. Being insoluble in water, it does not increase the iron content of water and degrade water quality. But at the surface of earth it can be naturally oxidised in presence of atmospheric oxygen and water, as shown in the following activating reaction



240 grams of pyrite (FeS_2) reacts with 224 grams of oxygen and 36 grams of water to produce 304 grams of ferrous sulphate (FeSO_4) and 196 grams of sulphuric acid (H_2SO_4). Ferrous sulphate, a water-soluble salt of iron, increases the iron content and sulphuric acid decreases the pH of water; both are detrimental to the water quality.

In a reaction system with 480 grams of pyrite, 500 grams of oxygen and 100 grams of water, TNRM of the three reactants are: pyrite: $480/240 = 2$, oxygen: $500/224 = 2.23$, water: $100/36 = 2.77$. When the reaction is complete, pyrite, having the least TNRM, will be exhausted when 52 grams of oxygen and 28 grams of water remain unreacted.

Pyrite-rich layers are generally situated under a thick sequence of soil and rocks. Depending on the position of the pyrite-rich layer with respect to the water table, some amount of ground water may permeate into them, but the quantity of atmospheric oxygen coming in contact of these layers is very small. So the quantity of ferrous sulphate and sulphuric acid produced by the oxidation of pyrite is very small and that depends mainly on the molar quantity of oxygen available in the reaction site, and most of the pyrite and much of the water present in the reaction system remain unreacted due to the dearth of oxygen. But mining activity, through excavation and removal of overburden, exposes to atmospheric oxygen and water the pyrite present in rock layers, waste heaps, mineral dump etc. The total quantity of sulphuric acid produced will depend on the TNRM of pyrite or water, whichever is less. For example, in a surface water body where pyrite is transported from waste dump, the quantity of sulphuric acid produced depends on the supply of pyrite in it, until the ratio of pyrite and water exceeds 20:3 (i.e. 240:36). Similarly, the acid produced in a waste heap rich in pyrite depends on the quantity of water leaching through it.

16.2.2 Constraints of Reactions in an External Reaction Site

An external reaction site (like a waste dump) largely behaves as an open system, because the precipitated water penetrates into it, reacts with activating and neutralising minerals, and flows out of the systems with the net quantity of pollutant or contaminant produced. In this case, the reaction system extends from the surface of the dump to the depth of penetration of water; and the reaction between a mineral and water will be restricted by the TNRM of water in the reaction system. For this reason, more pollutant or contaminant will be leached out from the waste dump in the rainy season than in the dry season.

Besides, the permeability of the waste materials also plays an important role – greater is the permeability, greater amount of water will penetrate into the dump and as a consequence, larger will be the TNRM of water in the reaction system. If the surface of waste dump is covered by fine grained materials of less permeability (like clay), a large part of water falling on will not penetrate into the reaction system. For this reason, clay can be effectively used in liners of waste disposal.

Constraints of Reactions in an External Reaction Site

An internal reaction site like a pond or lake may appear as a close system, but it largely acts as an open system. When a mineral particle is transported to such a reaction site, its outermost part will react with the water. The soluble pollutant thus produced will be dissolved and defused in the water, exposing a fresh surface for reaction until the whole particle is exhausted. Therefore reaction between water and an activating or neutralising mineral will be restricted by the availability of that mineral – the quantity of it transported in the water body. Other factors remaining same, greater is the distance of the surface water body from the waste dump, less will be the amount of reactants transported to it. The surface water bodies nearer to the waste dump will therefore be more polluted.

16.3 THE ROLE OF CLAY MINERALS IN ACTIVATING AND NEUTRALIZING REACTIONS

16.3.1 Clay Minerals as Activating Agents

For a substance to act as an activating agent, it must react with natural substances to produce one or more soluble substances that increase the cation and anion contents of water. For example, zinc sulphide is an activating agent as it produces highly soluble zinc sulphate which increases Zn^{++} into water. But the clay minerals rarely act as activating agents in nature, as explained below.

Each mineral is stable within certain ranges of pressure and temperature and a definite chemical environment. The minerals formed in a high pressure, high temperature and reducing environment deep inside the Earth's crust may be uplifted by some geological processes and brought to the Earth's surface, where the physico-chemical conditions are much different, characterised by lower temperature and pressure, higher free water and free oxygen. Because of these differing conditions, those minerals will produce new minerals that are stable under conditions at or near the surface.

As shown in Table 1.4 (Part I, Chapter 1), clay minerals are among the most stable minerals in the condition prevailing at the Earth's surface. Therefore they are not likely to react with water or atmospheric gases to produce other substances. Moreover, they are insoluble in water (though may create a colloid solution in water for their extremely fine grainsize), thus incapable of changing the water quality. One clay mineral may be transformed to another

by processes like diagenesis, low-grade metamorphism etc. but that does not involve liberation of harmful materials in nature. So they rarely act as activating agents.

16.3.2 Clay Minerals as Neutralizing Agents

As discussed in the internal structure of clays in Part I, many clay minerals have t-o-t-c structures. In these clays, the c-layer in between two t-o-t layers has a series of cationic sites with 12-fold coordination number. Some of those cationic sites are filled up by interlayer cations like Na^+ , Ca^{2+} , Mg^{2+} etc. while the others are vacant. The metallic pollutants and contaminants like Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} etc. enter the c-layer of these clays by substituting the interlayer cations or by occupying the vacant cationic sites. Thus the heavy metals and other cations can be removed by the clays from a solution. These clay minerals therefore act as neutralising agents that naturally reduce or tend to reduce pollution and contamination. The metal cation adsorption capacity of clay minerals can be enhanced artificially by organic complexation as well as hydroxyl interlayering and pillaring. In addition to removal of heavy metals and other inorganic cations, clay minerals can also remove from the water the organic cations present in waste proteins, biological toxins, antibiotics etc. Non-ionic organic pollutants, anionic contaminants present in fertilizers and pesticides and organisms like viruses can also be removed by clay (Churchman et al., 2006).

Leachates form by the interaction of rainwater with the waste materials of mine or industrial waste dumps. The constituents of the leachates depend on the compositions of the waste materials in the waste dumps, and some of them may be potential pollutants or contaminants of water. When the leachate flows over the ground surface, it passes through the soil and some of the dissolved substances present in it are removed by the clay minerals present in the soil. Thus fewer amounts of pollutants and contaminants reach the surface water bodies. Therefore the surface water bodies distant from the waste dump are generally less polluted or contaminated than those that are close to the waste dump.

Similarly, when a part of leachate percolating downward through the vadose zone passes through the clay-rich subsurface layers, the clay minerals remove a part of dissolved substances from it, preventing or decreasing the pollution or contamination of ground water.

The clay minerals present in the aquifer and the wall of surface water bodies may also remove some dissolved substances from the water and improve the qualities of ground water and surface water respectively.

These neutralising properties of clay minerals facilitate their use to resist water and pollution. Furthermore, the waste materials may be prevented from coming in contact with water by burying them under soil or covering them by a thick layer of clays – the absorption and swelling properties of clays resist

the penetration of water in the reaction system and significantly decrease the TNRM of water in it. For this reason, clays can be applied effectively to build barriers/linings that resist spreading of pollutants and contaminants from waste dumps, to clear waste water and leachate of the harmful cations, and to protect the soil of agricultural lands from the harmful effects of chemical fertilizers and pesticides. These applications of clays are described in the next chapters.

16.4 ENVIRONMENTAL DEGRADATION BY CLAYS

In order to have a comprehensive idea of the negative impacts of clays on the environment, the following two phenomena should be understood separately:

- (a) During the mining and beneficiation of CLAYS, environmental degradation may take place.
- (b) During the mining of ANY ECONOMIC MATERIAL (any metallic ores, non-metallic substances or fuel), the clays present in host rock, country rock and overburden may cause environmental degradation. The clay present in the waste dumps of construction sites or industrial areas have similar impacts on the environment.

Most clay mines are surface mines, in which the miner and/or his machinery work in an excavated void which is open to the sky. The surface mines are of following types:

Open-pit mine: In this type of surface mines, the overburden is removed from the mine and dumped to a disposal area. The desired material is worked from stepped horizontal benches. Each bench is separated from the adjacent benches by vertical shelves. The slope angle ranges 50°–70°. Since clay layers are softer than most materials and the exposed parts become very slippery in rainy season, a smaller slope angle is required to maintain stability of the mine.

Open-cast mines: They are surface mines in which the stripped overburden is not removed from the mine to be dumped in a separate disposal area, but is “cast” (i.e. hauled and dumped) inside the mine from where the desired material is already worked.

The following operations are carried out in the mining of clays:

- (a) Stripping of overburden, i.e. excavation and removal of the vegetation, soil and layers of sediments overlie the clay bed
- (b) Mining of the clay
- (c) Disposal of waste materials
- (d) Beneficiation of the clay, i.e. partial removal of impurities and giving it a desired form.

All types of surface mines, including the clay mines, have some negative impacts on the environment in each of the three stages of operation, as briefly explained below.

- (i) Stripping of overburden causes destruction of a large amount of vegetation, and loss of top soil. This severely affects the environment of the surrounding areas.
- (ii) During excavation of clay from the mine, especially in the deeper levels, a part of the aquifer may be removed, leading to loss of ground water through increased evaporation, and causing serious hindrance to groundwater circulation. It also increases the possibility of pollution of ground water by exposing the aquifer to the pollutants (Younger, 2003). Even when the excavation is not deep enough to reach the water table or affect the aquifer, it intercepts the surface runoff and interflow, leading to wastage of water and desiccation of surrounding surface water bodies (Mukhopadhyay and Ghosh, 2011a and references therein).
- (iii) The mine wastes, when dumped at a different place (i.e. in case of open pit mines), destroy more vegetation and top soil. If the waste materials contain any harmful chemicals, that may be leached out from the waste dump in the rainy season and pollute the surface water bodies and soil of surrounding areas.

In addition to the above environmental degradations that are common to all types of surface mines, the clay mines in particular may cause air pollution. Clays are finest of all sedimentary particles, and owing to their fine grain size, they are very light and easily airborne. For this reason, the fine clay particles are suspended easily in the air during mining and beneficiation. That may cause respiratory troubles and other health hazards to the mine workers and the inhabitants of surrounding areas. A detailed account of environmental degradation during clay mining and beneficiation is given in Chapter 8 of this book.

16.5 ENVIRONMENTAL DEGRADATION BY CLAYS FROM WASTE DUMPS

In any mining operation, overburden materials and tailings are disposed in the waste dumps. Many construction works necessitate excavation and removal of soil and sediment layers from a large area and dumping them to a nearby place. Clays are the major components of these waste dumps. Clays may also be present in some types of industrial wastes. Different components of the waste dump may have different impacts on the water, soil and air of the surrounding regions. The impacts of clays of the waste dump on the environment are given below.

- (i) Of all types of sedimentary particles present in the waste dumps, the clays are the lightest and most easily suspended into the air. The airborne clay particles may be carried to far-off places, and affect the health of the inhabitants of surrounding regions. Respiratory diseases such as *silicosis* can result from long-term exposure to clay dusts.

- (ii) Clay particles are easily transported from the waste dumps by air and rainwater, while the coarser particles are left back. The transported clay particles settle on the soil. They may block the soil pore spaces and absorb a considerable amount of infiltrated rainwater, and less amount of water is available for surface runoff, interflow and groundwater recharge. In addition, the moist clay particles form a cohesive plastic mass in the soil that hinders the lateral and vertical movement of water in the unsaturated zone. Less lateral flow of water brings about further decrease in the throughflow and interflow, contributing to desiccation of surface water sources. Decrease in the vertical movement of water, on the other hand, further decrease groundwater recharge that leads to fall of water table.
- (iii) A large amount of clay particles, when deposited on a small stream or pond, may block it or fill it up, leading to depletion of water sources.

Concluding Remarks

Rapid growth in the population and concomitant industrial development and urbanisation has given rise to rampant mining activities, establishment of new industries and extensive constructional works in different parts of the world. All these have brought about disposal of a huge quantity of waste materials, which are the sources of all types of pollutants and contaminants and are therefore serious threats to the Earth's environment. In this context, extensive researches are going on throughout the world to find out effective but economic means to prevent environmental pollution and contamination from the waste materials. Clays, owing to their stability, distinctive properties, abundance and easy availability in nature, may be applied effectively to overcome some of the appalling environmental problems coming from the wastes. Researchers are therefore increasingly depending on clays and clay derivatives to invent possible ways of pollution control. The utilization of a particular type of clay for the control of a particular class of pollutants or contaminant is gradually attaining its own maximum stage of development. With the passage of time, further industrial developments may give rise to new environmental threats or exacerbate the present ones, necessitating further researches for finding out new applications of the clays for environmental protection.

At the same time, growth of the civilization calls for a greater utilization of clays and its derivatives in the industries, and substitution of metals with them. This will give rise to increase of clay mining and associated environmental degradation, necessitating simultaneous researches for minimizing the harmful effects of clay mining.

QUESTIONS

1. Is it justified to use the terms environmental pollution, contamination and degradation interchangeably? Explain with examples.
2. Is it possible for a substance to act as an activating agent in a particular circumstance, and as a neutralizing substance in another? Cite suitable example in support of your answer.
3. In a waste dump, metallic sulphides react with rain water to form soluble sulphates, which leach out to pollute the surrounding water bodies. The TNRM of which reactant will be the main controlling factor in this activating reaction? Explain.
4. In a water body, metallic sulphides leach out from a nearby waste dump and react with water to form soluble sulphates and pollute the water. The TNRM of which reactant will be the main controlling factor in this activating reaction? Explain.
5. Explain why the clay minerals hardly ever act as activating agents.
6. Both clay mineral and CaCO_3 present in the rock layers or soil can remove sulphate pollutants from leachates. Which of these two neutralizing agents do you think is more appropriate from the environmental point of view? Explain with reasons.
7. What is the role of the swelling property of smectite clays in environmental protection?
8. An overburden dump comprises different materials like gravels, sands, silts, clays etc. of which air pollution is caused by clays. Which property of clays is responsible for it?

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