Filtration Removal of Americium, Cobalt & Cesium in Ob River Water Under Conditions of Increasing Salinity

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In this paper, Michael Boyer attempted to determine the magnitude of an emerging environmental threat: the flow of radioactive materials from industrial sites in the former Soviet Union to rivers and other bodies of water, which in turn empty into the Arctic Ocean. While such radioactive pollution is harmful regardless of its destination, the Arctic's precarious ecology is particularly vulnerable. Scientists have a poor understanding of this region of the earth; it is difficult to predict the fate of radioactive substances that interact with ice sheets and other features of the Arctic Circle. Furthermore, the Russian Arctic coast lies frighteningly close to Europe and North America.

Nevertheless, not all radioactive pollutants make it into the ocean. For one, there are a number of metals that water cannot dissolve. Other radioactive substances are reasonably soluble in fresh water but precipitate out of solution and sink to the seafloor when mixed with salt water. Boyer studied this phenomenon with three different radioactive substances and sought to determine which ones remained reasonably soluble as salinity increased. These pollutants represent a great worldwide threat, for they could pass from the freshwater Ob River to the saline Kara Sea without falling out of solution. Such substances would ultimately flow into the Arctic Ocean.

Boyer first tested the influence of increasing salt concentration on the solubilities of the three radioactive pollutants in Ob River water. He repeated the experiment using Hudson River water and, for his third trial, Ob River water that had been treated to remove molecules that might influence solubility. In all three tests, he observed clear differences among the three radioactive substances; some were far more responsive to the changes than others.

Glossary

•aliquot: Fraction of a larger sample.

•americium-241: One of the three radioactive isotopes that Boyer studied. Although included in the periodic table of elements, Am-241 does not occur naturally in the earth's crust. It is often produced when neutrons bombard the nuclei of plutonium atoms, another artificial element, and is often a byproduct of plutonium production in breeder reactors.

•anion: Negatively-charged particle.

•cation: Positively-charged particle.

•cesium-147: One of the three radioactive isotopes that Boyer studied. It is a major component of nuclear fallout. Since the Soviet Union detonated a large number of atomic weapons in the atmosphere before such tests were outlawed, Cs-147 pollution is of particular concern in Russia.

•coagulation: Irreversible process similar to that of flocculation.

•cobalt-57: One of the three radioactive isotopes that Boyer studied. Co-57 exists naturally, but is not dangerous unless processed through industrial or military means in concentrated form.

•complex: Short for complex ion, an ion (charged particle) that consists of a metal cation surrounded by a number of molecules or anions. Complexes of a given metal are generally more stable than the corresponding free metallic ion because the surrounding particles counterbalance its positive charge. In general, metal cations with larger ionic charges form complexes more frequently than those with smaller ones -- highly-charged cations benefit more from this "shielding." The study of the speed with which complex ions form is also important. No matter how great the would-be increase in stability from free ion to complex, the latter will not form in any observable concentration unless the metal cation and other particles come together at a reasonable rate. Polarizing power (see below) is the key to studying this mechanism.

•flocculation: Reversible coupling of multiple particles in suspension. As such a conglomerate grows larger in size, the random bombardment of water particles striking the unit will no longer be able to support it. The collection of particles would subsequently sink to the bottom, preventing them from traveling further. Boyer used a filter designed to collect all flocculation products larger than 0.2 μm in diameter.

•gamma rays: Specific type of radiation that all radioactive isotopes produce, each isotope emitting rays with a characteristic energy.

•ionic radius: Distance from the center of the nucleus of a given cation or anion to the boundary surface of the ion's electron cloud: the area in which electrons are most likely to be found. While cations represent metals that have lost one or more of their outer electrons, they still have a number of inner electrons.

•isotope: Sample of a given element (i.e substance whose atoms all have a specific number of protons) with a specific number of neutrons as well. Certain isotopes of a particular element can be stable while others are unstable (radioactive). For example, samples of carbon contain large amounts of stable carbon-12 (with six protons and six neutrons) along with small quantities of carbon-14 (with six protons and eight neutrons). This phenomena is the basis of the radiocarbon dating technique, allowing scientists to determine the age of artifacts and specimens with a reasonable degree of accuracy.

•μCi: Abbreviation for microcurie. A million μCi equal one curie, the fundamental unit of radioactivity. A curie corresponds to a certain number of nuclear disintegrations (atomic nuclei of one type being transformed into another) per second. Thus, the curie (and hence the μCi) is NOT a unit of mass because not all radioisotopes decay at the same rate. For example, consider a one gram of sample A along with ten grams of sample B. If sample A consists of an isotope that decays 100 times as fast as that in sample B, sample A actually contains ten times as many curies as sample B.

•micron: Millionth of a meter, abbreviated μm.

•polarizing power: Ease with which a cation can distort the electron density of a neutral molecule or anion, attracting the electrons toward the positive charge without taking them completely. As a result, the molecule or anion follows along, forming a complex ion (see above) with the cation. Polarizing power is an important factor in determining the rate at which a cation complexes. It is directly proportional to ionic charge (the number of electrons that a metal atom lost to become a cation) and inversely proportional to the radius of the resulting ion. With increasing positive charge, a cation attracts negatively-charged electrons more readily. Likewise, ions with a smaller radius must compress their charge into smaller volumes, increasing charge density and rendering them more powerful electron "magnets."

•ppt.: Stands for parts per thousand, a unit of concentration that Boyer uses to indicate the amount of salt in a given sample.

•radiation: Emission and transmission of energy through space in the form of particles and/or waves. These waves actually represent photons — massless particles without a charge. Radioactivity and radiation are not the same thing! Gamma rays (see above) represent a form of radiation, extremely high in energy, that results from radioactivity. However, other types of radiation (the photons produced when an electron drops from a high-energy orbit to a lower one, for example) do not.

radical: Neutral molecule with an unpaired electron. Radicals are often formed by radiation and are highly reactive.

•radioactive: Adjective applied to any isotope that spontaneously emits radiation (resulting from the decay of atomic nuclei). Thus, the description connects the concept of radiation with that of radioactivity.

•radioactivity: Spontaneous decay of an atom coinciding with the emission of radiation and often particles as well. Once again, radiation and radioactivity are not identical; refer to the definition of "radioactive" above.

•salinity: The amount of salt in a given sample of water. This is the variable in Boyer's experiment.

•UV: Stands for ultraviolet radiation, a component of the electromagnetic spectrum with photons that are higher in energy than those comprising visible light.

Background

Radioactivity results from the disintegration of atomic nuclei. In the familiar nuclear reaction that atomic bombs harness, atoms of uranium are bombarded with neutrons. This splits the uranium nucleus into two smaller nuclei representing the cores of lighter elements. However, a few neutrons escape to strike other uranium nuclei, propagating a chain reaction.

While the amount of energy produced in such a process is enormous, other nuclear reactions yield far smaller amounts of radiation. Boyer studied the effect of salt concentration in water (salinity) on the solubilities of three different radioactive isotopes — cesium-137, cobalt-57, and americium-241. Although these substances are incapable of producing a mushroom cloud, they are still extremely dangerous to living organisms. The atoms of all three isotopes contain unstable combinations of protons and neutrons. This renders them susceptible to nuclear decay, typically producing alpha or beta particles—dangerous types of radiation in their own right. However, a third stream of particles typically flows from the unstable nuclei as well: high-energy photons known as gamma rays. These are far more energetic than the two other particles that can stem from radioactive decay. Photons also lack electrical charge (unlike positive alpha particles and negative beta particles). As a result, it generally takes an eighteen inch slab of lead (surrounding a fallout shelter, for example), to absorb gamma rays completely.

However, such precautions are well worth the effort. When molecules come in contact with gamma radiation, the photons often strike electrons and transfer their energy to the negatively-charged particles. In many cases, this "boost" allows the electrons to escape the pull of the positively-charged nuclei that they normally orbit. This transformation changes the chemical nature of the molecules (now radicals) drastically. Because atomic and molecular structures are far more stable when all electrons associated with them are in pairs, the electron whose "mate" was ionized by the gamma rays will attempt to find another partner. Typically, this replacement comes from another molecule, forming another free radical. The resulting molecular transformations are often quite dramatic. For example, exposure to gamma rays is dangerous to life because their high-energy photons can disrupt the structure of DNA, usually causing unnoticeable cell death but sometimes triggering cancer.

The effects of gamma rays on molecules may be catastrophic for life, but they allowed Boyer to determine the amount of radiation in given aliquots of his original samples. He used a Gamma Counter, an instrument that measures the actual energy of molecules ionized by gamma radiation. Boyer tracks this figure rather than the rate at which the rays drive off electrons and the molecules are subsequently ionized because the device is able to distinguish between gamma rays produced by different radioactive isotopes. With this capability, Boyer could determine the precise amount of radioactivity associated with the cesium, cobalt, and americium isotopes in a single sample. Had this not been possible, he would have needed to use three times the number of aliquots—one set for each isotope. This complication would certainly have been time-consuming. A far more important problem with the alternative technique concerns the question of consistency among the three samples—how would a researcher be positive that they were truly identical except for the identity of the added isotope?

This question is of particular importance with the third experiment of Boyer's investigation. With all of his isotopes in the same samples, he could rest assured that they were surrounded by organic molecules that had been oxidized to the same extent. This concept is a complicated one, but it is based on the idea of radicals discussed above. The ultraviolet radiation knocks electrons out of hydrogen peroxide, which in turn react with dissolved organic molecules to break them into smaller fragments. Since these molecules were an important part of the metal complexes discussed in the glossary, irradiation of water with UV radiation is an excellent way to break up complexes and isolate the free metal cations. A look at the results confirms this.

Questions

1. Of the three isotopes that Boyer studied, americium-241 was the only isotope removed by filtration in any significant percentage (over ten times that of cobalt and hundred times that of cesium). This percentage was directly proportional to salinity in the sample of Ob River water that was not treated with UV-radiation. Considering the fact that americium has the greatest polarizing power of the three elements and consequently forms complexes the most readily, what does this suggest about the effect of salt on complexes? Can you suggest a logical explanation for this conclusion? Remember that all salts in solution consist of dissolved cations and anions.

Answer: Salts destabilize existing complexes, leading to their decomposition. The various cations "compete" with the original americium cations for the anions and neutral molecules that initially surround the radioactive ion, exposing the americium ions to water.

3. Consider Boyer's statement that "because the percentage of americium removed by filtration was unexpectedly high, the experiment was repeated." Does this reflect the intended nature of the scientific method? Explain

Answer: At the surface, clearly no. One undertakes an experiment to verify or refute a given hypothesis. The accumulation of knowledge is the most important result, not whether the investigator was right or wrong. Designing an experiment with the express intent of demonstrating a preconceived conclusion is a cardinal sin of science. However, Boyer likely based his statement on existing references and sought to verify a result that had already been documented. Nevertheless, he should have provided a specific reference to the study in question.

4. Should a 0.2 μm filter remove more or less sediment than a 1 μm filter? Examine Boyer's line graphs and determine whether or not this always held true in his experiment. What does your answer suggest about the validity of his results? Note the graph scales carefully.

Answer: A 0.2 μm filter should remove all of the matter that a 1 μm variety would, along with particles between 0.2 and 1 μm in diameter. While this was generally true in Boyer's results, he observed the opposite in two of the Cs samples. These data cast doubt on the rest of Boyer's results, but are not central to his conclusion. Despite their anomalous fluctuations, the percentages in question are still virtually nonexistent compared to the corresponding figures for americium, meaning that Cs ions will almost certainly proceed in solution from the Ob River estuary into the Kara Sea.

5. Based on Boyer's results, are anions more important than neutral molecules in the formation of americium complexes? Explain carefully.

Answer: No, neutral molecules appear to be more important. This is reflected in Boyer's UV results. In freshwater, filtration of regular Ob water removed less than 40 percent of the Am. By contrast, filtration of the UV-irradiated water removed more than ninety percent of the metal, indicating that the destruction of the neutral organic molecules had broken up the Am-centered complexes almost completely — without any salt at all! Indeed, the percentage of Am removed by filtration in the UV samples actually decreased as salinity rose.

Resources

Chang, Raymond. *Chemistry*, Fifth Edition. New York: McGraw-Hill Inc., 1994.

Pankow, James F. *Aquatic Chemistry Concept*s. Chelsea, Michigan: Lewis Publishers, 1991.