Phosphate Rocks: Sustainable Secondary Source for Uranium and their Agricultural Impact - 9481

Dr. David V. LeMone. Professor Emeritus, P.G.
Dr. Philip C. Goodell
Department of Geological Sciences
University of Texas at El Paso
P.O. Box 3, 500 West University
El Paso Texas, 79968

Dr. Arthur H. Harris, Professor
Department of Biological Sciences
University of Texas at El Paso
El Paso Texas, 79968

John W. Winston, Jr., Medical Physicist
Radiological Physics, Inc.
4333 Donnybrook Place
El Paso, Texas 79902

ABSTRACT

The current, ongoing, intensive development of the international phosphate industry is destined to impinge onto at least two major aspects of nuclear energy in the immediate future. The first contact will come in the evaluation of the economic viability and potential sustainability of sedimentary phosphorites as a secondary source for uranium. The second impact will be in the determination of whether or not there exists significant uranium contamination in the utilization of phosphate fertilizers on agricultural systems. There are no adequate substitutes for phosphatic fertilizers. Phosphorous derived from these fertilizers is absolutely essential for the maintenance, growth, and yield of crop plants as well as the survival of all living systems.

If the current (6.748 billion), let alone projected, global population (±9 billion, 2040) is without a continuing, uninterrupted, and increasing supply of this ubiquitous commodity for the agricultural system, the world will face certain global famine. The most severely impacted will be those emerging and third world tropical nation-states with phosphate-poor soil systems. The fundamental reason we have been able to feed the bulk of humanity today and avoid a predicted Malthusian future famine is in large part due to the use of phosphate fertilizers.

Accompanying the benefits of phosphate-based fertilizers are potentially serious side effects that need to be examined. Phosphate based fertilizers contain heavy metals, led by uranium. Some of the resulting problems are the questions of: the quantitative dimensions of uranium contained in phosphate fertilizers that is lost into the environment (soil and aqueous systems) and how, whether, and under what conditions does the metal enter the biosphere's food chain (animals, plants, and water). Therefore, the downside to the use of phosphate fertilizers is that the uranium in those fertilizers can be transferred to agricultural systems and subsequently to ground- and running-water systems. The potential resultant impact of this on plant life systems is and will continue to be subject to continuing research.

In view of the environmental consequences of continued reliance on fossil fuels, the shift to the extensive development of nuclear power seems inevitable. Given the current national and international conditions, it's necessary to carefully examine the political and economic ramifications of such a shift. Competing alternatives of wind (cost and reliability), solar (cost and size), and hydro (at near capacity) will not even

begin to substitute for the current fossil fuel usage (oil, coal, gas, tar sands, etc.). The only realistic source of utilizable energy, now and in the future, will have to be nuclear.

The secondary extraction of uranium has long been a tantalizing prospect for developing a sustainable source of the metal.[1,2,3] A number of phosphate rich nations have reassessed the prospect of such a development in Asia (e.g., China [4]) North Africa, (e.g., Egypt [5]) and the Middle East (Syria, Jordan [3]). The development of a secondary industry involving extraction of uranium from phophorite ores has a history of prior development in the United States with eight production plants in Florida and Louisiana.[3] However as a result of a drop in the price of uranium (yellow cake), these plants were forced to close.

If the sustainability of a uranium fuel supply is found to be a significant factor, the secondary recovery of uranium from phosphate processing provides a potential continuing source of the metal. The waste streams that result from the processes adapted for the secondary extraction of uranium from phosphate fertilizers also will require evaluation. This does not erase the potential and threatening political consequences involved in the potential illegal accumulation of available metal for clandestine and/or rogue military purposes.

The primary sulfuric acid extraction process of phosphate rocks results in the accumulation of phosphogypsum. For every ton of phosphoric acid produced five tons of phosphogypsum byproduct is being generated. Phosphogypsum is classified as TENORM (Technically Enhanced Naturally Occurring Radioactive Materials). This classification makes the commercial utilization of the byproduct (construction, etc.) without further treatment highly unlikely. All the legacy monuments as well as the currently generated accumulation of phosphogypsum waste will have to be dealt with. Volume and cost of transport make disposal to available commercial low-level waste facilities cost prohibitive. There seems to be no currently reasonable solution for the disposal of the phosphogypsum solid waste.

Regardless of what happens, any adjustment, political or legal, in relation to the phosphate fertilizer industry will have unintended and probable negative consequences. There is a pressing need to get ahead of the curve on this problem of uranium within phosphorites; it is not about to go away.

INTRODUCTION

This paper addresses some of the issues that are related to the indispensable use of phosphate fertilizers in agriculture. Two issues of interest evolve from this usage. The first and fundamental question is concerned with the potentiality of the phosphate rocks fertilizer extraction process as a sustainable secondary source of uranium; the second and related issue is the impact of process-related generated radioactive waste developed in byproducts, waste streams, and agricultural applications.

The initial consideration is the importance of phosphorous as an element and in maintaining life systems. Phosphate fertilizer usage in agronomy has and is preventing global famine. The sources and origins of phosphate rock ores are the next consideration. The processing of phosphate rocks is reviewed from the standpoint of direct application, thermal processing, and wet processing. Byproduct phosphogypsum is examined as well as is the usage of uraniferous phosphate rock-derived fertilizers. The problematic remediation of agriculture lands is reviewed. The anthropogenic accumulation of uranium and heavy metals from agriculture and military use is examined. A summary and a conclusion section follow these earlier segments.

PHOSPHOROUS AND LIFE SYSTEMS

Phosphorous (P) is the 11th most abundant element in the lithosphere. It makes up 0.09% of the Earth's crust. It typically is represented by an oxyanion (phosphate PO_4^{-3}) in organic molecules and inorganic mineral systems. Manning [6] points out that the popular assumption that the apatite minerals represent the dominant host for P is incorrect. Actually it is the phosphorous content in mineral feldspars that is the main reservoir of P in the lithosphere. Feldspars are the dominant minerals in an estimated 40 to 50% of crustal rocks. Phosphorous can be accommodated in the feldspar lattice by replacing tetrahedral silica in a coupled berlinite substitution with aluminum. Manning [6] states that the feldspar P_2O_5 content is normally 0.2-0.3% in continental crustal rocks, but may be as high as 1% in selected granites.

Phosphorous (P) is an absolutely necessity for plants and all other terrestrial life systems and, possibly, the element represents the key to development of extraterrestrial life systems. It is essential in the formation of RNA (ribonucleic acid), DNA (deoxyribonucleic acid), ADP (adenosine diphosphate), and ATP (adenosine triphosphate) of living organisms. Phosphorous occurs in other organic material, for example, in the form of the mineral apatite that involves the biomineralization of bones and teeth. The apatite in bones stores 80wt% of the P, 99wt% of the calcium, and 50wt% of the magnesium in the body and can redistribute these chemical reservoir elements on demand.[7] There is no substitute for this element.[6,8]

The deficiency of P in soil is a critical factor in agronomy. Deficiency typically results in either highly restrictive limitations or failure in crop production. To alleviate the absence and/or to increase the presence of the element, we use phosphate fertilizers in modern agronomy. In the broad sense, the utilization of phosphate fertilizers can be viewed as a fundamental survival tool for the modern nation-state. Its availability is currently a necessity for some nation-states.

Japan has a long history of utilization of phosphate fertilizers to solve some of their agricultural problems. Andosols make up nearly half of the upland fields and pastures in Japan. Andosols have high adsorption ability for phosphates. They are derived from volcanic ash and occur with amorphous allophane and imogolite in Japan.[9] Under comparable climatic conditions on the Pacific Rim and the Indian Oceanic areas volcanic ash soils similar to those developed in Japan can be expected. Another excellent example of phosphate poor soils is observable in the climates of the tropics. Climates in those regions can and frequently do produce phosphorous-deficient soils. Regrettably, For the most part these are the emerging and third world nation-states. These nation-states typically lack the financial basis and the basic infrastructure necessary for production of phosphate fertilizers for sustainable agronomy.

In many respects phosphate-fertilizers exist as one of the most effective barriers between our modern society and the arrival of a long predicted global Malthusian disaster. Today the global population is reliably estimated to be in excess of 6 billion individuals. The United Nations prediction [10] of 8 billion in 2020 and 9.4 billion in 2050 will signal even greater utilization of agronomic systems as well as requiring the higher productivity provided by phosphatic fertilizers.

The Malthusian population theory [11] is based on the concept of a developing geometric population growth versus an arithmetic increase in food production ultimately leading to global poverty and starvation which can be checked only by disease, high infant mortality, war, or moral restraint. This pessimistic theory has been largely dismissed as being unrealistic based on the reality of the continuing technical advances made in agriculture and food production. Regrettably, this apocalyptic theory of disaster could become a reality if the phosphate fertilizer system is significantly tampered with either legally or politically.

Among the other future consequences of global population growth, it may be reasonable to assume that potable water will become one of the most profoundly problematic future resources. A major related difficulty presented here is not for too little P but for the instance of too much soluble P resulting in the

element's overabundance in aquatic systems typically resulting in eutrophication. Eutrophication is definable as an excessive richness of nutrients, like phosphates, in a body of water (e.g., lake) that results characteristically in dense proliferation of life (e.g., algal blooms), the decomposition of which kills animal life (e.g., fish) by depriving it of oxygen. Filippelli [12] notes that with the anthropogenic loss of forestation and topsoil combined with increasing fertilizer use, the eutrophication of lakes and coastal areas fed by river systems will become more commonplace. Remediation of potable water will not only be costly (e.g., removal of unpleasant taste/odor, property devaluation etc.) but may also represent some serious public health risks (e.g., production and release of algal toxins, etc.).[13]

The most notable eutrophication source will likely be the nutrient P in the increasingly necessary utilization of phosphatic fertilizers to augment crop yields to meet the survival needs of the increasing human population. Reflections aside, it is clear that the world system of phosphate utilization must continue operating efficiently and unencumbered in order to avoid dire consequences in the future.

Given the probability of that scenario for water and enlarging on that view, the presence of soluble and potentially soluble uranium, rare earth elements, and other contaminant metals in phosphate fertilizers becomes a concern and is, perhaps, an even more serious challenge. This aspect supports the need for a serious evaluation of uranium recovery from phosphorites.

PHOSPHATE ROCKS AND FERTILIZERS

The primary sources of P are the mining, processing, and extraction of the world's supply of phosphate rocks. Dahlkamp, in his seminal study of global uranium ore deposits [14], recognizes phosphorites as one of his 15 fundamental uranium ore types. Stewart et al. [15] defines phosphate rock as an imprecise term describing all rocks that contain high concentrations of P-bearing minerals. Phosphorites are used as the general term for sedimentary phosphate ores of marine origin. Phosphorites represent the bulk of the ores used in the production of phosphate fertilizers.[16]

The term ore is commonly used loosely in literature; if properly defined, it should always carry with it the requisite "the mineral must be mined and/or processed for a profit." If it cannot be mined at a profit, it should simply be called a mineral deposit. Regrettably, it doesn't consistently work that way. The escalation of the price of uranium yellow cake (lows = ± $8; highs = ± $130/pound) over the past five years serves as an example. Former uranium mineral deposits in many global regions were automatically converted to ores with the change in price. The use of the term secondary "ore" deposit carries with it the connation that it has at least some potential profitability.

Minerals

There are nearly 400 phosphate compounds that have been compiled; however, relatively few are critical to natural systems. The most abundant phosphates are the apatite group minerals and the most common is fluorapatite (commonly called apatite). The apatite crystal structure allows the incorporation in its lattice of nearly half of the elements of the periodic table.[8]. Pasteris et al. [7] state that apatite is an ideal choice for skeletal frameworks in that two biologically abundant elements Ca and P are present. Additionally, P is contained in collagen that directs the biomineral's precipitation. Apatite is a "relatively sparingly soluble salt," making it a safe reservoir. The biological properties are conceivably best described after Pasteris and others as where mineralogy meets geochemistry and the biological sciences.[7]

Origin

Phosphatic rocks may be igneous (e.g., Russia, Brazil, South Africa), sedimentary (North Africa, Jordan, Florida), or secondarily metamorphic (India). Apatite is observable in nearly all igneous rocks where it occurs in volumes ranging from 0.1vol% to 1.0vol%. It is intimately associated with feldspars that are the continental crust dominant mineral species and suggest, by mass balance, that they are the host of 50-90% of crustal P_2O_5.[6]

The commonest and most extensive ores are sedimentary and marine in origin. Kratz and others [17] estimate that 87% of phosphate ores being processed are sedimentary in origin. The phosphorous contained in these phosphorites is syngenetically developed. The ores are typically very low grade with respect to uranium, which however, is enhanced during processing. Also resulting are major TENORM solid (phosphogypsum) as well as liquid wastes. Extraction of uranium from phosphorites is primarily regulated and overseen by the U.S Nuclear Regulatory Commission and/or its Agreement States under the Atomic Energy Act. They are responsible for licensing and regulating source material (uranium extraction) operations. The Environmental Protection Agency (E.P.A.) (e.g., EPA documents, [18,19]) has authority for the regulation of air emissions of radionuclides from the phosphate industry in general, including that associated with uranium extraction..

Mined phosphate ores are separated, milled, and processed once to several times to produce the variant utilizable forms and derivatives of phosphoric acid. Phosphoric acid and its further derivatives are highly transportable and serve innumerable purposes.[20] Approximately 90% of the mined ore is utilized in the production of various phosphate fertilizers. The remaining 10% has been processed for animal feeds, chemical industry, detergents, etc.

PROCESSING PHOSPHATE ROCKS

The aims of the production of processed phosphate fertilizers concentrates on: increasing solubility in the final product, increasing the amount of P to reduce costs, improving the physical character of the product to allow more uniform application of the product as well as greater storability, and, of course, improving production development with lessened energy cost.[21] The practice of utilization of direct application of less soluble phosphate rock as a fertilizer without chemical treatment has proven to have limited value.

Direct Application of Rock Phosphates (DARP)

Direct application of rock phosphates is the least costly application process, normally only requiring sizing in its beneficiation prior to use. The practice of using the direct application of sedimentary rock phosphates (phosphorites), as long as they have not been chemically processed, is an important feature of organic farming (e.g., organic phosphorite fertilizer from Gafsa, Tunisia).[6] The applied phosphorites normally lack any readily soluble phosphate salts and, therefore, rely on the chemical rhizospheric capability of the plant life system to break down and release the available phosphorous from the contained phosphate minerals and develop a calcium sink for the process.[6]

In selected cases rock phosphates represent a better product for plant recovery, thus allowing the utilization of phosphorites that are normally not desirable in the wet phosphoric acid extraction system and, as a natural system, it avoids not only the potential generation of excessive liquid pollutants but also the production of the solid phosphogypsum TENORM waste.

Certainly not all soils and crop systems are suitable for the direct application of phosphate rocks (DARP). The commonly used wet process sedimentary phosphorites are very complex due to their variant geologic origins and may contain unacceptable levels of heavy metals such as uranium. The level of knowledge of the environmental impact of DARP and the inherent level of risk involved, if proven significant, will require rigorous future evaluation of the benefits and problems of the application of raw phosphorites

versus the more readily soluble processed fertilizers on crop systems. Additionally, consideration of the usage of DARP depends on individual nation-state's financial capabilities, the involved physical and geo-demographic character of the targeted area, and national and international governmental policies and regulations that must be addressed.[22,23]

Uranium is not the sole hazardous elemental component observed in phosphorite ores. Van Kauwenbergh [23], in his cadmium study of some 17 global phosphate deposits, lists the highest assayed contaminant values recorded from a limited sample from these deposits. Potentially, these selected contaminants under ideal conditions could become available to the biosphere from DARP: arsenic (Sechura, Peru); cadmium (Hahotoe, Togo); chromium (174 mg/kg from Djebel Onk, Algeria); lead (Mussorie, India); selenium (Gafsa, Tunisia); vanadium (Taiba, Senegal); and uranium (390 mg/kg from Minjing, Tanzania). Phosphate rocks occur with high percentages of fluorine (up to 3%). Utilization of these require process defluorinization, particularly prior to usage in animal feedstocks.[23]

Phosphate Rock Processed Fertilizers

Sedimentary origin phosphorites consist of on the order of 80% of the current mined production of phosphate rocks. The standard treatment of phosphate rock is utilization of wet processing acidulation, normally using sulfuric acid and less commonly nitric acid. In cases in which pure phosphoric acid is a requirement the Electric Furnace (or Thermal) Process is the preferred extraction method.[13,21] The costly high grade thermal phosphoric acids account for only 2% of production and are for non-agricultural purposes for those industries requiring high purity acid.

The 'wet process' for the production of phosphoric acid (H_3PO_4) commonly refers to the dissolution of phosphate rock by sulfuric acid (H_2SO_4).[16] The acidulation solid byproduct formed as a resultant of this process is phosphogypsum ($CaSO_4 \bullet 2H_2O$), It is filtered out from the acid and retains ±30% of the U-238 present in the phosphate rock. The remaining ±70% of the U238 is retained in the liquid which is further concentrated by evaporation to form superphosphate (NSP) with an enrichment of ±150% of the initial U-238 (18-20% P_2O_5).[17] The superphosphate acid concentrate treats further phosphate rocks to form triple superphosphate (TSP) fertilizers (40-48% P_2O_5). The addition of ammonia (NH_3) forms ammonium phosphate (46-48% P_2O_5).[17]

The standard for acidulation has been sulfuric acid because of cost and availability. Phosphogypsum is a byproduct waste from this process. For every ton of phosphoric acid produced from sulfuric acid acidulation there are five tons of phosphogypsum produced.

A good example of the resulting TENORM waste problems is illustrated by a Croatian phosphogypsum repository (currently at ±4 Mm^3, capacity 20 Mm^3). It has been developed on a river floodplain 5 km south of an operational fertilizer plant in central Croatia.[24] The triple superphosphate and ammonium phosphate fertilizers from the plant are produced by the wet process method from ores imported from North African sources. Slurries of water and phosphogypsum are pumped to the repository and the water is recycled back to the plant forming a closed circuit system.[24] The Radiation Protection Unit of the Institute for Medical Research and Occupational Health (Zagreb) has had an extensive radioecological program since 1948. They report that nearly all the [226]Ra from processing is incorporated into the phosphogypsum since its chemical properties are similar to that of calcium in gypsum ($CaSO_4 \bullet 2H_2O$). The site has been and is continuously monitored for possible increases in soil and groundwater radiation. [226]Ra has a high potential for biological damage in that continuous irradiation over many years may produce bone sarcomas. The results of site testing indicate that the effective dose for [226]Ra does not exceed that which is recommended by the World Health Organization (WHO).[24]

The major legacy phosphogypsum repositories are found in association with the long-term wet process phosphatic acid production from the Florida ores. EPA classifies phosphogypsum as TENORM solid waste, which makes it unsuitable as a new or alternative substitute for other uses. The logical use of phosphogypsum as a potential alternative for commercial gypsum has been examined and rejected because of its radioactive and other hazardous materials in United States and the European Union. Current solutions to this problem seem to revolve around either the construction of monolithic tumuli or oceanic dumping.

The 'nitrophosphate wet process' utilizes nitric acid for acidulation of the phosphate rock. This results in the formation of a nitrophosphate solution and crystallized calcium nitrate $(Ca(NO_3)_2)$. Ammonium carbonate is added to calcium nitrate to form ammonium nitrate and calcite.[17] The nitrophosphate solution that has been concentrated by evaporation, has ammonia added to it. Potassium chloride is also added. The resultant product is then granulated to form a NPK (nitrogen-phosphorus-potassium) fertilizer. [17] One particular advantage of the process is that no bulky development of phosphogypsum results.

Kratz and others [17] of the German Federal Agricultural Research Centre (FAL) report a number of FAL and literature analyses of uranium concentrations (mg/kg) in straight phosphate mineral fertilizers with their origin clearly established. Their ranges and means are useful and yield some ideas; however, at this initial stage of data accumulation, it is difficult to amass enough samples of these fertilizers to produce statistically meaningful results. The problem of culling out the data from earlier times when uranium was being extracted may be a problem. An additional potential problem is the difficulty encountered in trying to interpret uranium analytical variations that are due to the inherent geological complexities of depositional and environmental history of the analyzed phosphorites.

Sattouf and others [25] have developed the application of uranium $R(^{234}U/(^{238}U)$ and strontium $R(^{87}Sr/(^{86}Sr)$ isotope ratios for tracking the fate of uranium through the processing of phosphate fertilizers from phosphate rocks. In effect the ratios act as a fingerprint. These ratios from phosphate rock to phosphorous fertilizer remain virtually the same and can be identified in four groups from their rock phosphate samples: 1. Kola Peninsula; 2. Senegal and Togo; 3. United States of America; and 4. Middle East (e.g., Syria) and North Africa (e.g., Morocco, Tunisia, Algeria) [25]

Determination of the quantity of uranium that will accumulate or be lost in the soil requires focus on the soil's origin and accumulation, biological-physical-chemical characters (e.g., soil fertility, clay content, grain size, Eh and pH values, etc.). Given the accumulation, plant genotypic differences regulate the uptake, transport, and storage of uranium. Schick and others [26], based on low uranium transfer factors, are of the opinion that crops grown on uranium contaminated soils are not as important to the metal entering the food chain as is leaching of uranium to groundwater aquifers and runoffs. As may be surmised, remediation of agricultural soils, given the areal and volumetric magnitude of the problem, is not only prohibitively expensive but also patently futile. The solution to this impasse lies back at the manufacturing process originating the phosphate fertilizer and the removal in that process of the uranium content.

This assumption is at least partially consistent with conclusions reached in phytoextraction studies.[27] The search in all phytoextraction studies for the various contaminants, primarily heavy metals, is for the hyperaccumulator plant. The hyperaccumulator plant is supposed to accumulate 50-500X more metal than commonplace plants. Additionally, the target hyperaccumulator plant should have a high growth rate and produce a high biomass. While hyperaccumulator plants have been found for Mn, Ni, and Pb, there is no hyperaccumulator plant for uranium.[27] Those plants tested have demonstrated slow growth rates and/or low biomasses. Furthermore, there is the disposal problem inherent within this as within other radioactive disposal systems. How will the ultimate radiometric waste products be sequestered in such a fashion as to

prevent its re-entrance into the biosphere? The apparent available choices for disposal would seem to include: a non-food product (wood cardboard), incineration, landfill, and recycling (phytomining).[27]

URANIUM TOXICITY

Uranium is a toxic heavy metal that naturally varies widely in natural soils (0.79 – 11mg kg^{-1} [26]. Accumulation of uranium by anthropogenic activity, such as the application of phosphatic fertilizers, has been reported in the A horizon of agricultural soils globally. The questions posed are, "What represents a permissible risk level of uranium for humans and what is the potential biological availability of that uranium and its daughter products that enter man by the water he drinks, the air that he breathes, and/or the animals and plants he ingests?"

Busby [28] as well as other researchers has been reassessing the radiological and biochemical impact of uranium ionic and sub-micron particles on human health. The major concern continues to be potential geonomic damage. Busby [28] has suggested that the model utilized by the ICRP to obtain the absorbed dose calculations (energy per unit mass) is incomplete. Schmitz-Feuerhake and Bertelt [29] in agreement, point out that the original population base line was drawn from a population of uranium miners, people living near uranium mines, and workers processing uranium. In these areas the average particle size is on the order of 5 microns. The importance of ultra-fine size particles, which could result in a tremendous dose enhancement, is not adequately addressed. Moreover, they feel that all risk groups are not proportionally represented (e.g., fetuses, embryos, children, elderly, etc.).

Chemical binding of uranium to DNA has been observed since the 1960s.It is frequently cited as the cause of what is referred to as anomalous genotoxicity and often called 'heavy metal toxicity.' Busby [28] cites from literature the fact that very strong binding exists between DNA phosphates and uranium. Most importantly, he states that the probability of photoelectric absorption of gamma and X-rays is roughly proportional to the fourth power of an element's atomic number (or Z number). It should also be noted that the photoelectric attenuation depends strongly on the atomic number of the absorbing material and it is proportional to the Z number cubed.[30,31] The absorbed gamma and X-rays within the genetic material uranium re-emits that energy as short-range photoelectrons. Uranium (Z=92), therefore, is the most powerful absorber (and re-emitter) of natural background radiation that exists in nature. It should be remembered that normally in living systems the Z number does not exceed 30. Heavier elements in the human system, when present, are typically in trace amounts.[32] Iodine (Z=53) that concentrates in the thyroid and blood system is an apparent needed heavier element. It is possible that thyroid may act as a human radiation detector that produces hormones for the body to neutralize radiation effects on the body.[28] It may be a reflection of a necessary evolution in the human species.

Uranium is ubiquitous in our environment and builds up in human and other living systems because of its affinity for tissue components, DNA, and nervous systems. Busby [28] cites the practical use of photoelectric enhancement in X-rays, which has been known since late forties; iodine (Z=53) and gold (Z=79) are examples.[28] What has been called "heavy metal" toxicity and associated carcinogenicity is possibly in large part due to uranium in the natural system of the Earth. Heavy minerals are similar only in mass. They are not chemically, toxicologically, or radiologically similar. Toxicity increases with Z number; Busby [28] uses Group II Metals as an example (i.e., Mg (Z=12), (Z=20), Sr (Z=38), Ba (Z=56)). We have long used the activity in finely divided heavy metals for industrial catalytic reactions (e.g., Pd (Z=46), Pt (Z=78), Ag (Z= 47)).

If the interaction cross-section per atom for gamma and X-ray photons were roughly proportional to the fourth power of the atomic number Z, then the effect between the uranyl and calcium ion would be on the order of 500-fold. The resultant photoelectric enhancement caused by the natural background absorption may be the causative source of anomalous radiobiological toxicity also so-called 'heavy metal

toxicity.'[28] The addition of uranium to the natural background by either use of uraniferous phosphate fertilizers or weathered depleted uranium ordinance is not to be desired.

It would be incomplete to deal with uranium toxicity on the human body if the question of radiation hormesis (aka radiation homeostasis) was avoided. The hypothesis is that chronic low doses of ionizing radiation are beneficial, stimulating the human organism repair mechanism that protects against disease.[33] The National Research Council, National Council on Radiation Protection and Measurements, and U.N. Scientific Commission on the Effects of Ionizing Radiation (UNSCEAR) do not accept the concept based on the fact that there is insufficient data available to clearly support the position. They maintain that the continuation of the linear no-threshold model (LNT) must be followed, not the viewpoint proposed by radiation hormesis. The LNT model in essence states that the damage incurred by ionizing radiation is linear or directly proportional to all dose levels. This position is in direct conflict with the concept of the establishment of a lower level of radiation below which it is harmless.[33]

SUMMARY

The direct application of raw phosphorites with variant reactivity, chemical composition, and physical properties have been considered, utilized, and examined as they have been tried as phosphate fertilizers. One of the major aspects of such use is the embedded risk of possible unintended consequences. This direct application can result in the addition of hazardous contaminants to that agronomic system. The contaminants, notably arsenic, chromium, cadmium, selenium, and uranium, occur both in direct and processed fertilizers, and present a risk to be considered. An additional problem with processing, especially in animal feeds, is the presence of up to 3% of the anion fluorine.

It is the availability of these elements in modern agronomy and, consequently, the potential transferability of these elements to the biosphere that must be considered as we continue to utilize raw phosphorites and processed phosphate fertilizers. Remediation of vast areas of contaminated agricultural cropland is cost prohibitive. The possibility of the application of either a phytoextraction method or a down-blending system is at best problematical. Governmental regulatory action may well be perceived as necessary. The increasing requirements for the partial extraction of uranium content as well as other contaminants in these fertilizers will significantly shift the economics of secondary uranium extraction from phosphorites. Uranium recovery could also offset the processing costs.

The last two years of gyrations in the uranium (yellow cake) market that reached highs of $130/0.454 kg (lb) in July of 2007 has enabled the reevaluation of the economic feasibility of the secondary extraction of uranium from phosphate fertilizers. The International Atomic Energy Agency has forecasted the possibility of a doubling of power from nuclear power plants by 2030.[34,35,36] The market fluctuations will continue and will be dependent on the keen perception by commodity traders of the current supply and future availability of the metal. The planned development and sustainable power generation of new nuclear plants on the Pacific Rim, Indian Ocean, and Asia already clearly illustrate some of the global supply problems.[3]

China has planned to increase their nuclear energy from 8.7 GW (2005) to 14 GW (2020) which will require an annual increase from 1,150 Mg in 2005 to 6, 450 Mg in 2020.[4] Australia delivered its first uranium to China in November of last year.[4] China views the extraction of uranium from phosphate rocks as having two positive aspects: domestic nuclear industry supply and minimization of contamination of agricultural soils.[4] The reported shortfall in India resulted in the delay in the construction of 14 planned plants as well as operational curtailment. That difficulty has apparently been altered in December with an agreement being reached between Nuclear Power Corporation of India and AREVA, the French national company, to supply reactors with uranium.[34] With an expected increase in competition for the supply of the metal becoming critical with the activity globally, it is possible that we

could see a reversal in the "No Nuclear Reprocessing Carter Doctrine." Such a reversal could see the emergence of economic MOX-fueled systems; however, it would have no effect on the phosphorite contaminate problem.

CONCLUSIONS

In conclusion, the combination of what is an apparently limited and potentially unstable supply of uranium in the reality of an expanding global nuclear power system will force some substantial changes. The economically driven uranium renaissance will continue with private and nation-state exploration and exploitation entities vigorously seeking to secure sustainable supplies of the metal anywhere in the world. There will be, dependent on politics, an active and continuing domestic reevaluation of the use of MOX fuels, most probably within the next five years. The current somewhat limited pilot plant level of extraction of uranium in the processing of phosphate rock for fertilizers is undergoing serious consideration in a number of nation-states. Industrial grade plants could offer a potentially sustainable long-term supply of the metal.

Nation-state geopolitical concerns and emerging unease over the potential of uranium from phosphate-based fertilizers also may aid in setting in motion the movement to an accelerated global adoption of the secondary uranium extraction process. Restriction of the free flow of these fertilizers will be politically disastrous for those who are responsible, for it is guaranteed to have a negative global impact in the unacceptable form of limiting food supply and the generation of consequent famine.

Those engineers and scientists with technical competence in nuclear waste management who are available nationally and internationally have the ethical responsibility to seriously address the problems produced by the beneficial application of phosphate fertilizer. This is exemplified by aqueous and edaphic contamination, eutrophication, and phosphogypsum waste utilization or disposal. It is necessary to get ahead of the curve on these problems before our society is called to account for our actions.

In relationship to security problems, the use of solid phosphogypsum TENORM waste as a radioactive dispersal device (RDD) is impractical.[3] The potential of sufficient accumulation of the metal from secondary byproduct extraction of phosphates seems to be equally impractical in the construction of a nuclear device. The accumulated processed uranium byproduct would have be separated by mass either by the construction of a costly gaseous diffusion plant or by the instillation of a system of cascading ultracentifuges. In construction and operation, neither one of these processes would remain unnoticed for any length of time.[3]

The reality of developing the extraction of uranium from phosphate rocks into a secondary ore source ultimately depends on two things: the current economy and, lacking an effective international political/enforcement control, nation-state governmental regulation and policy. Operational nuclear power plants represent the kind of infrastructure investment that commits host nation-state governments to supporting their continuing operations, even if the economy slows down. Solving the problems of monitoring, control, and disposal of phosphate-fertilizer-derived radioactive waste is not only in this society's interest but, more importantly, its responsibility. This area of nuclear waste management might not be as spectacular as working on the fuel cycle, designing a new generation reactor, or planning operational nuclear powered desalination plants, but it may ultimately turn out to be even more critical in the future.

Finally, it would seem reasonable to predict that the secondary separation of uranium from fertilizers derived from phosphate rocks will be adopted by nation-states because of sustainability needs, economics, and good environmental stewardship.

REFERENCES

1 WISE Uranium Project, 2008. Uranium Recovery from Phosphates, 3 p. < www.wise-
        uranium.org/purec.html> (Last update May 9, 2008).
2 Brand, R. A., 2007. Connection between Phosphate Fertilizer production and the Uranium Fuel Cycle,
        International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads
        and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.
3 LeMone, D. V., P. Goodell, S. G. Gibbs, and J. W. Winston, 2008. Uraniferous Phosphates: Resource,
        Security Risk, or Contaminant, Phoenix Rising; Session 35, General Issues in Low-Level
        Radioactive Wastes, Waste Management 2008, 15 p. (8476)
4 Hu, Z. Y., H. X. Zhang, Y. F. Wang, S. Haneklaus, and E. Schnug, 2007. Combining energy and
        fertilizer production – vision for China's future, International Symposium Protecting Water
        Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium,
        Braunschweig, Germany.
5 El-Sankary, M.M., 2008. The Egyptian Phosphorites: a Review, 26 p.
6 Manning, D.A.C., 2008. Phosphate Minerals, Environmental Pollution, and Sustainable Agriculture,
        Elements, v. 4, p. 105-108.
7 Pasteris, J.D., B. Wopenka, and E. Valsami-Jones, 2008. Bone and Tooth Mineralization: Why Apatite?
        Elements, V. 4, p. 97-104,
8 Oelkers, E.H. and E. Valsami-Jones, 2008. Phosphate mineral reactivity and global sustainability,
        Elements, v. 4, p. 83-87.
9 Yamaguchi, N., A. Kawasaki, and T, Iiyama, 2009. Distribution of uranium in soil components of
        agricultural fields after long term application of phosphate fertilizers, Science of the Total
        Environment, vol. 407, p. 1383-1390.
10 United Nations, Department of Economic and Social Affairs, Population Division
        <http://esa.un.org/unpp/>
11 Malthus, T. R., 1798. An Essay on the Principle of Population, London.
12 Filippelli, G. M., 2008. The Global Phosphorous Cycle: Past, Present, and Future, Elements, v. 4, p.
        89-95.
13 Foy, R. H., 2005. The return of the Phosphorous Paradigm: Agricultural Phosphorous and
        Eutrophication, in J.T. Sims and A.N. Shapely (Eds.) Phosphorus: Agriculture and the
        Environment, Monograph 46, ASA-CSSA-SSSA, p. 911-939.
14 Dahlkamp, Franz J., 1993. Uranium Ore Deposits, Springer-Verlag, Berlin, 460 p.
15 Stewart, W.M., L.L. Hammond, and S.J. Van Kauwenbergh, 2005. Phosphorous as a natural resource
        in J.T. Sims and A.N. Shapely (eds.), Phosphorous: Agriculture and the Environment, Monograph
        46, ASA-CSSA-SSSA, p. 3-22.
16 Harben, P. W. and M. Kizvart, 1996. Industrial Minerals, A Global Geology: Industrial Minerals
        Information, Ltd., Metal Bulletin PLC, London, 462 p.
17 Kratz, S., F. Knappe, J. Rogasik, and U. Funder, 2007. Uranium Balances in Agroecosystems,
        International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads
        and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.
18 Environmental Protection Agency (EPA), 1998. Background Information Document. Statistical
        Procedures for Certifying Phosphogypsum for Entry into Commerce, as required by Section
        61.207 of 40CFR Part 61, Subpart R, National Emission Standards for Hazardous Pollutants,
        EPA 402-R-98-008
19 Environmental Protection Agency (EPA), 2007. Radiation Protection, Rad NESHAPs Program
20 Jasinski, S.M., 2006. Phosphate Rocks in 2006 Minerals Yearbook, U.S. Geol. Survey, Reston, Va.
21 Leikam, D.F. and F.P. Achorn, 2005. Phosphate Fertilizers: Production, Characteristics, and
        Technologies, in J.T. Sims and A.N. Shapely (Eds.) Phosphorus: Agriculture and the
        Environment, Monograph 46, ASA-CSSA-SSSA, p. 23-50.

22 Food and Agriculture Organization of the United Nations (FAO), 2004. Use of Phosphate Rocks (PR) for Sustainable Agriculture, Fertilizer and Plant Nutrition Bulletin 13, Joint Publication of FAO and the IAEA (International Atomic Energy Agency), Rome.

23 Van Kauwenbergh, S. J., 1997. Calcium and other minor elements in world's resources of phosphate rocks, Fertilizer Soc. Proc. No. 400, The Fertilizer Soc., York, UK.

24 Bituh, T., G. Narovic, J. Sencar, and M. Bronzovic, 2009. Radioactive contamination in Croatia by phosphate fertrilizer producers, Journal of Hazardous Materials, 162, p. 1199-1203.

25 Sattouf, M., S. Kratz, K. Diemer, J. Fleckenstein, O, Rienitz, D. Schiel, and E. Schung, 2007. Significance of uranium and strontium isotope ratios for tracking the fate of uranium during processing of phosphate fertilizers from phosphate rock, International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.

26 Schick, J., S, Schroetter, M. Lamas, M. Rivas, S. Kratz, and E. Schnug, 2007. Soil/Plant interface of U, International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.

27 Haneklaus, S. and E. Schnug, 2007. A Critical evaluation of phytoextraction on uranium contaminated agricultural soils, International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.

28 Busby, C.C., 2007. Biochemical and Physical aspects of Uranium Toxicology, International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.

29 Schmitz-Feuerhake, I. and B, Bertelle, 2007. Radiological aspects of uranium contamination Uranium Balances in agroecosystems, International Symposium Protecting Water Bodies from Negative Impact of Agriculture, Loads and Fate of Fertilizer Derived Uranium, Braunschweig, Germany.

30 Khan, F. M. 2003. The Physics of Radiation Therapy, Lippincott, Williams and Williams, Philadelphia, Pennsylvania, 560 p.

31 Attix, F. H., 1986. Introduction to Radiological Physics and Radiation Dosimetry, Wiley – VCH, 587 p.

32 Wright, A. E., 1992. Medical Physics Handbook of Radiation Therapy, Medical Physics Publications, Madison, Wisconsin, 74 p.

33 Wikipedia, 2009. Radiation Hormesis, 3 p., <http://en.wikipedia.org/wiki/Radiation_hormesis>

34 Gopalan, N. and M. Hadi, 2008. Pluging in to Uranium's Glowing Future, Wall Street Journal, v. 252-43, p. B-10.

35 IAEA, International Atomic Energy Agency, 2001. Analysis of Uranium Supply to 2050, STI-PUB-1104, I.A.E.A, Vienna, 112 p.

36 IAEA, International Atomic Energy Agency, 1989. The Recovery of Uranium from Phosphoric Acid, IAEA-TECDOC-533, IAEA, Vienna, 104 p.