Uraniferous Phosphates: Resource, Security Risk, or Contaminant – 8476

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ABSTRACT

The escalation of the price of uranium (U) yellow cake (summer high = $130/0.454 kg (lb) has called into question the continuing availability of sufficient stockpiles and ores to process. As was developed during the years following World War II, the establishment and maintenance of a strategic inventory is a reasonable consideration for today. Therefore, it becomes critical to look at potential secondary resources beyond the classical ore suites now being utilized. The most economically viable future secondary source seems to be the byproducts of the beneficiation of phosphoric acids derived from phosphate ores.

Phosphorous (P) is an essential nutrient for plants; its deficiency can result in highly restrictive limitations in crop productivity. Acidic soils in tropical and subtropical regions of the world are often P deficient with high P-sorption (fixation) capacities. To correct this deficiency, efficient water-soluble P fertilizers are required. The use of raw phosphate rocks not only adds phosphate but also its contained contaminants, including uranium to the treated land. Another immediate difficulty is phosphogypsum, the standard byproduct of simple extraction. It, for practical purposes, has been selectively classified as TENORM by regulators. The imposition of these standards presents major current and future disposal and reutilization problems. Therefore, establishing an economically viable system that allows for uranium byproduct extraction from phosphoric acids is desirable. Such a system would be dependent on yellow cake base price stability, reserve estimates, political conditions, nation-state commitment, and dependence on nuclear energy.

The accumulation of yellow cake from the additional extraction process provides a valuable commodity and allows the end acid to be a more environmentally acceptable product. The phosphogypsum already accumulated, as well as that which is in process, will not make a viable component for a radiation disposal devise (RDD). Concern for weapon proliferation by rogue nation states from the byproduct production of yellowcake is an unlikely scenario. To

extract the fissile U-235 (0.07%) isotope from the yellowcake (99.3%) requires the erection of a costly major gaseous diffusion or a cascading centrifuge facility. Such a facility would be extremely difficult to mask. Therefore, from a diminished security risk and positive economic and environmental viewpoints, the utilization of a phosphoric acid beneficiation process extracting uranium is desirable.

INTRODUCTION

Two subtypes of phosphorites (Florida and Idaho) are classically recognized. The Idaho (Phosphoria) subtype is typified as shallow marine typically deposited either as outer (distal) shelf margin or shallow marine nearshore. The central Florida (Land Pebble District) stratiform deposit is the result of the reworking and re-exposure of phosphoritic mineral apatite to repeated inundation by uranium bearing seawaters during numerous transgressions combined with subsequent leaching and reprecipitation. Uranium concentration is thought to be due to synsedimentary extraction of U from seawater. Phosphorite U grades are normally variable and are very low grade; this combined with the difficulty encountered in beneficiation and extractive metallurgy currently prevent phosphorites from becoming primary U ores except as by-product (wet-process phosphoric acid). Eight plants for the recovery of uranium from the system have been built in the United States since 1976 (Florida and Louisiana). Current status of these plants is regulatory and market sensitive.

The nuclear waste management problems associated with phosphorites include phosphogypsum stacks as exemplified by the Land Pebble District of Florida. Most recently (7/12/07) there have been legal proceedings taking place in Huelva, Spain, to cease the operations of the Fertiberia fertilizer plant. The problems include the Fertiberia phosphogypsum stacks as well as a major phosphogypsum tailings-dam failure. Greenpeace (3/19/07) has been demanding classification of Huelva as a radioactive installation. The limits for radon emissions from phosphogypsum stacks represent another problem. Phosphogypsum, despite uranium daughter products being partitioned into it, hardly qualifies as a component for a radiation disposal device (RDD).

Tropical and subtropical third world countries are among those nation-states most desperate for water-soluble P fertilizers. Realistic economics prevent them from importing high quality water-soluble P fertilizers. Direct application of special grade phosphate rocks can be used as has been reviewed by the UN Food and Agriculture Organization. [1] What limits nationally or internationally need to be set for heavy metal and radioactive content of the fertilizers as well as special grade phosphate rocks needs to be standardized? The US Environmental Protection Agency (EPA) has revised the National Emissions Standards for Hazardous Air Pollutants (NESHAP), which has been codified as subpart R of 40CFR part 6l.

The sustainable security of lifetime food and potable water supplies is the primary basic requirement of the Earth's human population. Human life does not exist without the presence of both of these fundamental survival necessities. Any disruption or curtailing of the supply and availability of these requirements has catastrophic results with an ultimate loss of life within days. Negative manipulation of either of these two fundamentals qualifies as a heinous, inexcusable crime against humanity.

Conversely, over the past years we have positively manipulated the food supply with the application of such widely variant things as: the long-term phosphate usage in fertilizers for increasing crop yields; the more modern cold pasteurization (irradiation) of food products for their conservation, especially in the global equatorial and tropical areas; and the selective treatments for the control of agricultural pests by irradiation in addition to long term chemical utilization. The disruption of any of these positive changes will have a profound effect on food supplies. When this manipulation is political or economic in its origin, it is, at best, reprehensible. Large national and multi-national organizations and corporations involved in such actions must be prosecuted, especially if loss of life can be specifically attributed to their dealings.

The importance of phosphorous is that there is no substitute for it in agriculture. Phosphates, therefore, are a critical non-metallic ore vital to the production of food. Phosphates contain varying amounts of impurities, including uranium. These impurities are separable during the process of beneficiation. Therefore, the question that emerges is, "What economic, environmental, and political considerations, if any, are necessary to made with reference to the exploitation and extraction of uranium from uraniferous phosphates?"

STATEMENT OF THE PROBLEM

The basic problem that is encountered with uraniferous phosphates is that the wastes from phosphate rocks act as a treatable secondary byproduct source for uranium. The uranium in the phosphate ores can act as a potential resource, security risk, or contaminant. Phosphates are not unique in their ability to act as secondary uranium byproduct resources. The oil shales (e.g., Green River Formation), tar sands (e.g., Athabascan [Canadian], Venezuelan), and even the black shales (e.g., Chattanooga, Antrim shales) all contain extractable uranium. The global importance of uraniferous phosphates is in their utilization as an essential plant nutrient and a critical component for agricultural crop fertilization yields. In a world of over six billion individuals requiring the basic necessity of a sustainable food supply, phosphate's importance is recognizable without need for discussion. The specter of another modern, dark reapplication of the Malthusian population theory of geometric population growth versus an arithmetic increase in food production is not an unusual predictive doctrine given the apparent statistical realities of global capacity. Hopefully, there is not a non-cinematic "Soluent Green" in our future.

Phosphate's beneficial character, as stated before, is moderated by the presence of hazardous elements in the form of heavy metals and radionuclides. Phosphates are applied in three basic modes: as crushed ore [1], triple phosphate application without uranium extraction, and triple phosphate application with uranium extraction. The solid waste products of phosphate treatments are phosphogypsums.

The fact that the recoverable end product of uranium extraction can be yellowcake uranium oxide also can be positively considered to be a potential stockpile resource for future utilization in nuclear energy production. Conversely, it also presents a hazard should the nation-state processing the ore lack legitimate entry into the global yellowcake commodity market based upon shifting national geopolitical and clandestine considerations. The potential for

producing significant quantities of yellowcake in order to process it for U-235 production for fissionable nuclear devices would seem to be highly unlikely. However, the usage of the processed material as Nuclear Radiation Dispersal Devices ("Dirty Bombs") is another aspect of the problem from the question of security internationally [2,3].

The question of contamination is two-fold. The first is the consideration of the potential utilization of raw phosphate rocks either in direct application to agricultural soils or as triple phosphate application without the extraction of uranium. Uranium in a majority of pedological situations has the capability of developing soluble ions in the soil that can be utilized by the agricultural plants growing on it. The then-transferred ion results in becoming a link of the human food chain. Uranium and other elements, particularly heavy metals, may have, dependent on abundance and chemical state, significantly adverse consequences to human health. [1] The second contamination consideration is the disposal of the phosphogypsum and the liquid byproduct components resulting from the extraction of uranium from processed phosphate ores.

To address the problems encountered concerning the various aspects of phosphates, it is useful to examine the history of phosphate usage and production, the consideration of its variant geological origins, and its extraction processes and economics.

PHOSPHATE PRODUCTION CHARACTERISTICS

Approximately 90% of phosphate production goes into fertilizer manufacture; the remaining 10% is utilized in such areas as detergents, animal feeds, food and drink products, surface metal treatment, etc. The great majority of phosphate production is from sedimentary rocks. However, early in the history of phosphate utilization, guano in the form of bird and bat excreta, was the sole and highly sought after source of agricultural calcium phosphates (e.g., Christmas Islands south of Sumatra in the Indian Ocean, Carlsbad Caverns, etc.). Additionally, there is some magmatic deposit production (coarse crystalline apatite) as exemplified by the Kola Peninsula, Russia, and Kiruna, Sweden. [4]

The United States Geological Survey (USGS, open file) lists over 1600 phosphate mines, deposits [Open-File Report 02-156A&B], and occurrences in the US Geological Survey's Open-Files report 02-156A&B. [34] It is more useful to examine the major occurrences of this non-metallic ore. To this purpose Harbon and Kizvart [4] recognized 24 major phosphate deposits globally.

In North America this would include the two major United States occurrences: the Permian Phosphoria Formation of Idaho, Montana, Wyoming, Utah, and Nevada and the Miocene phosphates of Florida and North Carolina. There are two major phosphate deposits in Mexico. The first is associated with Jurassic impure limestones in the Zimpan, Hidalgo, area near Mexico City. The second Mexican phosphate development is observed along the western Pacific coastal margin of Baja California state. These Cenozoic deposits are believed to be due to the rich life developed by upwelling and its mixing of cold Pacific waters with the southeasterly flowing warm California current waters. Phosphates are more concentrated in the southern part of the Baja California Peninsula. In South America the northern Peruvian deposits in the Secura Desert, despite little production to date ($\pm$ 12,000 metric tons [t] P_2O_5), are categorized as world-

class. [5] These Upper Miocene pelletoidal phosphate deposits are associated with diatomites, tuffs, and a few thin sandstone beds. Undeveloped Lower Miocene phosphates also are noted in Icon state, Venezuela. [4]

Africa's major sedimentary phosphate deposits crop out along the western Atlantic coastal margin of Africa and swing northward and eastward to the middle northern African Mediterranean coast. The southernmost of these is in Togo, located on the African Gulf of Guinea, as a 32 km belt of phosphates within a Lower Eocene basin. The next major phosphate deposit is to the north in Senegal on the western bulge of Africa, which produces from Eocene calcium phosphates. Western Sahara and Morocco to Algeria and Tunisia completes the northwestern phosphate belts of Africa. Deposits range in age from the Upper Cretaceous to the Lower Tertiary. Three major Moroccan producing areas have been identified in the 320-km long northeastwardly trending belt of Upper Cretaceous and Eocene sediments. Morocco, which also administers the Western Sahara, is the major producer in Africa ($\pm$ 8420 thousand t P_2O_5). [5] The major import source for America is Morocco. Similarly aged Tunisian and Algerian phosphates are of lower grade and more difficult to process. [4]

The Middle East production is recorded in Egypt, the Negev Desert, Jordan, and Syria. These phosphates are primarily of Upper Cretaceous age, with some phosphates of Lower Tertiary in age being recorded in Jordan. Jordan is the major producer in the Middle East ($\pm$ 2450 thousand t carbonates and quartzites. Phosphates are confined to bluish green stromatolitic beds with pinching and swelling ore zones. The 700 thousand t P_2O_5 produced in India [5] are not sufficient for the Indian subcontinent requirements. [4]

Kazakhstan Lower Cambrian deposits are observed in Central Asia. Similarly aged Lower Cambrian production is developed in China (Yunnan and Lao Kay) and in Korea and Viet Nam also. Australian production comes from the Middle Cambrian of the Georgina Basin. Chinese production is the highest in eastern Asia and Oceania at 2500 thousand t P_2O_5. [4,5]

Phosphates occur in two general geographic alignments in Harben and Kizvart's analysis [4]: a trade-wind belt and an equatorial belt. [4] The trade wind belt extends from Equator to almost 50° latitudes. Upwelling cold, nutrient rich waters rise and bring nourishment to the marine plants and subsequently to those animals grazing on the plants until they reach such abundance that they produce phosphorous-rich organic debris on the seafloor bottom. Trade-wind deposits tend north-south (e.g., Baja California), whereas equatorial systems tend to align east-west (e.g., Middle East, Venezuela. The North American Phosphoria Formation and the Florida/North Carolina deposits are utilizable domestic examples for phosphate origin and deposition.

URANIFEROUS PHOSPHATES OF THE MIDDLE EAST,

The Tethys oceanic system in the Late Mesozoic and Early Cenozoic developed the conditions necessary for major phosphorite deposition. This body of water separated Africa and the Middle East from Eurasia. It has been influential in determining the geology of North Africa, southern Europe, and southwest Asia, which includes essentially the Middle East region of today.   The Tethys Ocean was exceptionally productive for the formation of sedimentary

phosphate deposits from the upwelling of ocean currents onto flooded cratonic or continental margins.   This region is responsible for a significant portion of the phosphate production of the world. Most of these phosphate deposits are of Mesozoic Late Cretaceous age, although some are of early Cenozoic age. Abundant phosphates are found in Syria in the Sawwaneh Formation, in the Amman Formation in Jordan, and in the Phosphate Member in the upper part of the Mishash Formation in southern Israel. [7] These three Late Cretaceous examples range in age from Late Campanian to Early Maastrichtian.

Uranium concentrations in the Middle East phosphate deposits are variable and unpredictable. In the Negev in southern Israel, Gill and Shiloni [8] estimate between 350 and 3,900 t of U per square kilometer of mineable phosphate, with a maximum of 100 ppm in the ore zones. They demonstrate a high positive correlation between U and P, and offer an equation of that relationship: U ppm = 9.0 + 4.0 (phosphate %) for their data. Enriched zones formed by secondary reworking and enrichment of uranium. They state, "The possible remobilization of uranium out of phosphorites poses obvious potential environmental hazards for land use and the toxic contamination of groundwater resources." [8]

Soudry and others in 2002 [7] document the hexavalent or oxidized character of these deposits, and wrote "In addition, a lower % U(IV) in the analyzed granular phosphorites is coupled with a lower rare earth elements, (REE)/P_2O_5 and Y/ P_2O_5 ratios, a higher Cd and Zn concentration, less negative Ce (Ce/Ce*) and Eu (Eu/Eu*) anomalies, a lower HREE (Dy-Er) enrichment, and a lower F/ P_2O_5 and higher CO_2/F ratio in francolites." These reported details [7] can be used on a comparative basis elsewhere. Enrichment in REEs is noted.

Jordan is endowed with large phosphate resources, as emphasized by the last portion of the title of a recent article, 'The formation of a south Tethyan phosphorite giant'. [9] Jordanian phosphate is known to contain uranium, and regional springs have anomalously high radioactivity. [10,11,12] Uranium efflorescences appear on phosphatic layers in exposures created by a dam construction near Yarmuk. Jordanian phosphate is shipped to India, where uranium is extracted. [21]

Syria has large phosphate resources and also significant production. Phosphate rocks are reported to have approximately 100 ppm U. [14] The utilization of airborne radiometric studies has proven useful for phosphate and uranium exploration. [25] Syria reports recovery of uranium from phosphate ores in addition to a power point presentation tour of that extraction plant. [15]

Egypt has many areas which produced phosphate over a long history. Khatera and others in 2001 [16] report on a radiological assessment of the natural radioactivity at the Abu Tartur deposit. [20] Aly and Mohammed, 1999 [17] report successful recovery of lanthanides from the giant Abu Tartur phosphate deposit. These ores are averaging 0.11% REE, but only 25 ppm U. Nitric acid was used as a leaching agent instead of sulfuric acid; REE and fluorine recovery was successful. They report that "the produced fertilizer would pollute the environment less with radioactive materials due to the low uranium content." In addition, this phosphate rock is a better source than monazite of rare earth products in that thorium is not present in these phosphate ores. The safe disposal of Th can be a significant environmental problem.

Algeria reports [18] efficient recovery of U at the phosphoric acid plant at Annaba. Acid contains between 40 and 300 ppm U, depending on the source rock. The authors state "Uranium not recovered will be lost forever and, furthermore, it may be a source of pollution for soil and plants when the phosphoric fertilizer spreads to the soil."

PHOSPHATE CLASSIFICATION AND ORIGIN

Dahlkamp [19] in his classic treatment of uranium ore deposits recognizes phosphorites as one of his 16 types; he further subdivides them into two major subtypes: Phosphoria and Land Pebble. He notes that the phosphorites, which accumulate on marine continental shelf's, can be broadly categorized into two zones: an outer bedded uranium-richer phosphorite sequence and a proximal nodular phosphorite zone. The outer shelf margin zone is frequently observed to be associated with black shale facies and a noticeable lack of carbonates. Conversely, black shales and fine clastics are uncommon in the proximal nearshore nodular phosphatic facies. Additionally, the land pebble phosphate type results partly from the reworking, subsequent secondary solution, and final reprecipitation of uranium leading to the enrichment of the primary phosphate deposition.

The Phosphoria (Idaho) type (e.g., Phosphoria Formation Montpelier, Idaho) Permian Phosphoria Formation underlies an area on the order of 335,000 km^2. Its dark, phosphatic, argillaceous Meade Peak Member ranges from 85 to130 m in thickness. Total resources are on the order several million t with grades averaging 60 to 200 ppm. Lack of infrastructure, accessibility, transportation difficulties, mining development complexities, and political climate have negated development to this time. The Florida model has been a much more profitable enterprise for the many of the reasons that the Phosphoria Formation failed to develop. [5,26]

The Florida Peninsula is the south-southeastern extension of the continental mainland of North America. It is an interesting site for the study of the geochemistry of uranium. The peninsula rests upon a more extensive Florida Platform. The Cenozoic peninsular sedimentological history of deposition is particularly useful to understanding the deposition and development of phosphatic ore deposits. The basement or base of the broad Florida Platform consists of rifted, left behind Avalonian or Gondowanaian cratonic crust that connected with Laurentia (North America) after the opening by sea floor spreading of the Atlantic in the late Mesozoic. This product of the Wilsonian cycle of closing (Paleozoic Appalachian orogeny) and opening (Atlantic Ocean) of oceans left the Gondawanaian Florida Platform jutting out into the otherwise straight northeastwardly directed margin of the newly created eastern cratonic boundary of eastern North America. The presence of the Florida platform created an oceanic current circulation disruption between the newly evolving Gulf of Mexico and the northwestern Atlantic Ocean. This circulatory disruption led to the conditions that allowed the peninsula to become the host for the accumulation of phosphatic-enriched sediments. [4,26]

The Florida Peninsula may be divided physiographically into three zones north to south. South of the North American cratonic Northern Highlands is the narrow Northern Proximal Zone, succeeded to the south by an extensive Central mid-Peninsular Zone, and completed ultimately to the south by a Southern Distal Zone. From a geological perspective, the important physiographical subdivisions are: the Ocala Upland along the northwestern coast, succeeded to

the south by the Central Florida platform, and ultimately to the south by the Okeechobee Basin. The deeper waters of the Gulf of Mexico culminated in a major upwelling along the western margin of the Florida Peninsula. The entire peninsula was flooded during the Miocene with the exception of the Ocala Upland. The resultant upwelling currents had to flow south around the upland, across the Central Florida Platform, and then around the then-higher standing Okeechobee Basin. The Central Florida Platform is where vast amounts of phosphate rock were deposited and subsequently reworked. Atlantic upwelling in the nearby Southeast Georgia Embayment was occurring at this same time, resulting in the deposition of related substantial phosphate resources observed there. [4,26]

The related Atlantic upper continental margin coastal embayments to the north of the Florida-Georgia area have histories that do not precisely parallel those of Florida Platform. The Atlantic upper continental margin systems are best characterized by the North Carolina Miocene Pungo River Formation's cyclic phosphate sedimentation in the Onslow and Aurora embayments. [22,29] Strong environmental depositional indicators for fourth-order cycles in the formation include three distinct clay-mineral suites (Kaolinite, proximal muddy quartz sands [precedes sea-level lowstand]; illite/smectite deposited in the phosphatic facies; and authigenic dolomite containing palygorskite and sepiolite [restricted to organic-rich dolomitic sediments, highly dysaerobic conditions associated with highstand and the formation of the condensed section]). [27]

Riggs and others [29] integrating biostratigraphy and Sr isotope data have constrained the ages of four third-order depositional sequences recognized in the Aurora and Onslow embayments. These data derived from their studies have developed an idealized phosphogenic sequence stratigraphy reflecting six stages of sea-level change and their expected depth and sedimentation pattern. Four of these North Carolina continental margin episodes are recognized. The three oldest episodes are dominated by primary phosphate origin. The Pliocene-Quaternary youngest episode sediments contain phosphate reworked from upper two episodes. The Miocene episodes (older to younger) include: 1. Aquitanian (23.3-21.6 Ma); 2. main Miocene phosphogenic event, Burdigalian - Langhanian (21.0-14.8 Ma) and; 3. Serravallian – Tortonian (12.7 – 7.1Ma). [29]

Sedimentary phosphate rock deposition is caused by upwelling of cold oceanic currents providing nutrients to phosphate-producing organisms dwelling on continental shelf environments. Deposits can be extensive on the shallow shelf, and they are available when the sea level is lower. Facies relationships are commonly associated with black shales and the consequential low oxygen concentrations that are necessary to accumulate the organic matter. Phosphorous is then concentrated by bacterial-related processes. [22] Uranium in this reducing environment would be in the tetravalent or +4 state and can reasonably substitute for calcium in apatite. Solution and reprecipitation of minerals that can rework and enrich deposits may take place. Sedimentological and geochemical reworking oxidized the deposits and uranium is subsequently hexavalent or +6. This state of uranium may not have a specific mineralogical expression.

The timing of the accumulation of the major phosphates of the world is not accidental. Accumulations coincide with major climatic and plate tectonic events resulting in major shifts in

the oceanic current patterns and cyclic sea-level changes. Stille and others [28] utilizing oceanic Nd isotopic data from marine phosphorites have been able to develop a persuasive sequence of evolving paleocurrents from the lower Jurassic (180 Ma) to the present for the Atlantic and Tethyan seawaters. [28]

Additionally, these accumulations are occurring at times in which the biotas are in significant environmental and radical evolutionary stresses. The Precambrian Indian phosphates are intimately associated with stromatolites of probable algal origin. The phosphates of eastern Asia and Australia occur at the time of the unique environmental conditions and explosive evolution of the Lower and Middle Cambrian. The late Mesozoic phosphates of the world are tied not only to the opening of the Atlantic and resultant paleogeographic reconfiguration (e.g., Morocco-Western Sahara, Florida, etc.) but also to the radical biotic changes that are happening in the biota (e.g., foraminifera, other invertebrates, etc.).

PHOSPHATE ECONOMICS

Very large and significant phosphate deposits exist and are being exploited for fertilizer in mining operations worldwide. In Florida, major economic phosphate deposits occur in the Miocene to early Pliocene Hawthorn Group. [22]

Florida contains some of the earliest larger deposits, which were mined; its exploitation continues today with reduced production. In 1985 for instance, 50E+06 t (million t) were mined, and 5 E+09 t (billion t) was the estimated near surface reserve. [5] The current US reserves (Florida and Phosphoria) are estimated to be at 1.2 E+12 t. Global reserves are estimated to be 18 E+12 t. [23]

Total world production of phosphate was 142 E+06 t with 44.3 E+06 t of P_2O_5 content. The four highest phosphate rock producers in the world are: China (30.7 E+06 t), United States (30.1 E+06 t), Morocco-Western Sahara (27 E+06 t), and Russia (11 E+06 t). The top three producers account for 62% of the global production. Morocco-Western Sahara provided 99% of the phosphate rock imported into the US. [5] In 2006 the US phosphate production dropped to a 40-year low. China surpassed the US as the largest global phosphate producer in 2006. [5,23] Imports resulted in the closures of a two phosphate mines, four fertilizer plants, and one mine temporarily shut down.

URANIUM IN PHOSPHATE ROCKS

An example of the geologic versatility of uranium is the fact that phosphate rock invariably contains small amounts of U, approximately 50 ppm. Some deposits are enriched in U, at 100 ppm. Under exceptional situations the U contents may reach 250 ppm. The source of the U can only be seawater; the phosphate minerals scavenge uranium out of the seawater. Altschuler [24,22] notes several other chemical elements often enriched in P, such as V, Se, Mo, F, and rare earth elements.

These totals are not very large numbers. It is well to remember that during the summer of 2007 the spot price of U reached as high as $130/0.454 kg (lb). As of this December date, it is at

$93/0.454 kg (lb), a far cry from the years in which the value fluctuated in the $8/0.454 kg (lb) range. This shift in commodity price plus the present operational excellence of the nuclear industry has done much to restore confidence in utilizing uranium-based power plants. [30] The major political and environmental recent attitudinal shift is in reaction to global warming and its clean air component. As nuclear power offers the only logical and reasonable solution to this environmental quandary, its fuel, uranium, is destined as a commodity to not only currently enjoy a renaissance but also look forward to a promising future.

The Central Florida Phosphate District is and has been a major uranium producer. Phosphoric acid is manufactured from the rock, and the uranium goes into the acid, from which it can be readily extracted. The N Florida-S Georgia phosphate district has significantly lower U contents, in comparison to the other Florida deposits; additionally, the southerly ones are 50% higher in F, Se, Mo. [26]

MINERALOGY

Marine phosphorite-related uranium deposits are dominated by cryptocrystalline-fluro-carbonate-apatite containing syngenetic uranium substituting for calcium according to Dahlkamp. He further notes that carbonates in general and Al and Ca-Al phosphates have a negative correlation with uranium concentration. Conversely, he notes a positive correlation between relatively high potassium and uranium concentrations. Secondary concentrations of uranium as observed in Florida are due to sedimentological reworking or weathering, not ore-related alteration. Harben and Kizvat [4] list six additional phosphate minerals with their typical environments (e.g., Brushite, found in guano in Algeria and the Caribbean; Fluorapatite, in igneous rocks, bedded marine, metamorphic rocks, and detrital sediments; etc.)

PHOSPHATE ORE EXTRACTION:

The extraction of phosphorous into a usable form from raw phosphate rock involves several steps dependent on the accessory minerals and elements in the original mined phosphatic ore. These are summarized nicely by the IAEA in their document on the recovery of uranium from phosphoric acid. [11] Beneficiation initiates dependent on mineral and chemical content. Accessory minerals such as quartz, feldspars, cherts, clays, micas, calcite, and dolomite are removed or lessened by such processes as, washing, crushing, floatation, centrifuging, magnetic separation, and calcining at $800^{o}C+$. Crushing, particular with reference to hard ores, is necessary to allow reaction with the acid utilized (e.g., $CaO: P_2O_5$ ratios greater than 1.6 require excessive acid). One t of processed P_2O_5 produces 5 t of gypsum that could develop into a major national/international TENORM issue or at best a present a disposal problem. Calcining may be necessary to remove accompanying carbon that can cause foaming in the acidulation process. High content of magnesium, iron, or aluminum can be problematic as a colloid issue in the beneficiation process.

The resultant treated ore is dissolved in sulfuric acid and may produce superphosphate, triplesuperphosphate, phosphoric acid, or superphosphoric acid. Phosphoric acid is popular in that it can be transported in tankers and is a starting material for many industrial processes according to Guilbert and Parks' evaluation. [26] Uranium recovery from the product stream (fertilizers, detergents, etc.) is based on solvent extraction. [34] Several systems are possible; the

DEPA-TOPO process has proven to be the best technology according to the IAEA nearly 2 decades ago. [11] Its process is: 1. Acid preconditioning and gunk removal; 2. First cycle extraction and strip; 3. Raffinate post treatment; and 4. Second cycle extraction, strip, and uranium precipitation. WISE [30], using current data, estimate of 3700 t of uranium could be recovered. That estimate is based on processing 66 E+06 t of concentrate (from the 142 E+06 t phosphorite mined) with a recoverable content of 100 ppm uranium. Marine phosphorite deposits account for 80% of the world's fertilizer output, and 70% of that total is converted into the wet process phosphoric acid, the basis for the current uranium extraction process. Historical operating costs for recovery of uranium from this process ranged between 22 and 54/0.454 kg (lb)based on uranium commodity market price. [30]

PHOSPHOGYPSUM

Phosphogypsum is the calcium sulfate byproduct of the wet-acid process used to produce phosphoric acid from phosphorite concentrates. According to EPA estimates, for every t of phosphoric acid produced, 4.5 t of phosphogypsum are produced. Phosphoric acid, as previously stated is an ideal industrial fluid in that it is liquid form and capable of being transported (e.g., tankers, railcars) and is the initial point of a host of different industrial systems (e.g., food, metal finish, uranium recovery, etc.). Separation of phosphogypsum in the wet-acid process is as slurry, which is pumped into a disposal rectangular disposal site. As the phosphogypsum precipitates out workers dredge the center and use the crystallized phosphogypsum as an outer wall/dike. Over time the slurry precipitates build a vertical stack. A 1989 EPA survey recorded 63 of these stacks covering from 12.4 to 1829 hectares (5 to 740 acres) with stack heights ranging between 3.1and 61 m (10 and 200 ft). [31] A subsequent 1993 mine site visit was made to the IMC Fertilizer, Inc. Four Corners Mine. It was prepared for inclusion in the 1994 Technical Resource Document on extraction and beneficiation of ore minerals (vol. 7, Phosphate and Molybdenum). [33]

The major problem is a perceived radiation hazard. The EPA phosphogypsum samples had concentrations of uranium (10 times the soil background) and radium-226 (60 times soil background). The samples vary in uranium and significantly in radium-226 from location to location and within individual stacks. The resultant statistical quandary makes the reutilization of phosphogypsum a virtual impossibility. [31] Radon-222, the gas decay product of the radium-226, is the radiation hazard. The risk is that gypsum dust with radionuclides coming from these stacks could become embedded in the food chain, presenting a hazard to life. [31]

Two notations concerning aspects of research methods and methodology have appeared in the Federal Register (FR). The first in 1996 was in response to   The Fertilizer Institute's (TFI) petition of a reconsideration of the 40 CFR Part 61, subpart R decision of June 3, 1992, this revised the final rule for the National Emission Standard for radon emissions from phosphogypsum stacks. It deals with the disposition of phosphogypsum for research and development and the methodology to determine the average radium-226 concentration for phosphogypsum removed from stacks (FR, vol. 61, no. 90, p.20775 – 20779). In 1999 in the Federal Register (FR) the EPA sets limits on radon emissions from phosphogypsum stacks in response to TFI's critique of their risk assessment studies. Phosphogypsum limits for R&D were raised from 276 to 2756 kg (700 to 7000 lbs), then current sampling requirements for

phosphogypsum used indoors were eliminated, and the sampling procedures for phosphogypsum removed for other purposes was clarified (FR, vol.64, no. 22, p.5573 – 5580). [30.31,32]

This is not a minor problem. The total amount accumulated from 1910 to 1981 is on the order of 7.7 E+09 t. Since 1981 it has been ranging from 40 E+06 t to 47 E+06 t annually. Disposal options include dumping it back into the sea, burying it, or leaving it as tumuli stacks. It would seem that there should be some incoming governmental funding for finding an adequate usage for this currently unwanted resource (e.g., some area of agriculture and/or construction). It certainly does not represent a potential source for uranium and recycling would not be a realistic option. The risk figures and assumptions that establish the limits of radon in phosphogypsum need to be revisited. Is phosphogypsum a real danger? If it is such a danger, then it should be addressed as a global standard by the IAEA. The solution then, of course, would be that all phosphogypsum is required to have its uranium and its daughter products extracted and recovered.

CONCLUSIONS AND RECOMMENDATIONS

The occurrence of phosphorites in the sedimentary column indicates the presence of dramatic changes in sedimentation character and volume, paleo-oceanic current systems, and normally a positive increase in the paleoenvironmental conditions for life. As phosphorites represent the ore for manufacturing modern high-yield fertilizers, they are an indispensable part of the today's global agricultural system. The social and economic impact and significance of this naturally occurring basic raw material is without parallel. The product of the wet chemical system, phosphogypsum, presents the difficulty. There has to be a use found for the billions of t of legacy phosphogypsum that we have accumulated and will be producing in the future. Phosphoric acid production must continue and grow in the future unless we are seeking the resurrection of famine and the prophecy of the Malthusian doctrine.

With reference to security and terrorism, is this a virtual non-problem? It is going to be very difficult to assemble enough yellow cake to begin processing it for recovery of the 0.7% U-235 in the uranium. In order to do that, you would have to have separation facilities such as the gaseous diffusion system or a cascading ultracentrifuge system. There is no reasonable way to hide such systems and their activities. As the uranium has been chemically separated to a yellowcake, it is without the usual suite of daughter products. Therefore, it is not going to be especially adequate as a RDD device versus the utilization of spent nuclear fuel. In fact, it would seem to suggest that an extracted yellow cake makes a poorer RDD component than one made with daughter products derived from standard ores and/or the milling process. There would seem to be no promise in using phosphogypsum as any sort of an ingredient for a RDD. RDDs are fundamentally by design a psychological weapon rather than an effective destructive devise.

The process of recovery of uranium from phosphorites would be a realistically useful process with minimal security risk. The adoption of the process produces a commercially viable secondary commodity and, more importantly, removes the threat of soluble uranium entering the food chain. The practice of using crushed phosphorite rock on soils in the tropics carries with it some inherent risks of contamination, which have been noted by the UN's Food and Agricultural Organization. [1] Third world countries in these tropical regions are subject to periodic famines. The question of their utilization of available raw phosphates with potentially problematic

contaminants is irrelevant. These nation states have neither the economic capability nor the infrastructure to support phosphoric acid plants, let alone the ability to adopt processes to extract uranium from untreated phosphoric acid. They will require international guidance and realistic assistance most logically should come through United Nation agencies.

At first, the unsubstantiated rumors of over-the-counter turnkey uranium phosphate extraction plant systems being available in Brussels does not sound reassuring. Should these phosphate-uranium-extraction systems, considering this Byzantine geopolitical world we find ourselves in now, need to be for the foreseeable future carefully monitored and documented? Probably not worth it as, realistically, the components for the system as well as the science and technology are available. Attempts to prevent proliferation of this technology would be unenforceable in the world we live in. Adopting the viewpoint that the process represents a diminished security risk, it becomes a realistic international option. On balance, this combined with the positive side of the extraction technique which produces a commercially valuable byproduct resource and yields an environmentally highly desirable end product makes the beneficiation process extracting uranium desirable.

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