Bauxite, alumina & aluminum radioactivity – *ZEGOR® Remedy for safe metals* (3rd page - radon effect)

For decades, studies on mining/extraction of numerous metals (e.g., aluminum, copper, titanium, gold or rare earths interlaced with radioactive traces) have warned of mounting radiotoxicity in tailings and solid waste and resulting long-term environmental damage. Given concerns over occupational and end-product safety, there have been repeated calls for technological innovation and improved management of radioactive waste. A remedy for NORM[1] in bauxite/laterite-kaolinite processing streams (or in those of other metal-bearing minerals), is SETF's ZEGOR® Process. It separates out co-located radioactive materials as co-products, thereby avoiding their build-up in process tailings, virtually eliminating human and environmental hazards, and cutting radiotoxicity in finished aluminum and alloy products. To demonstrate, ZEGOR® separates out elemental uranium from oxides by first converting to gaseous uranium chloride and then isolating the uranium chloride from, say, aluminum, nickel, or cupric gaseous chlorides in the processing stream. Distilled gaseous chlorides of aluminum, nickel, or copper *can be iteratively cleansed of any residual radioactive trace materials* followed by reduction to elemental powders as discussed below. Using (CO,Cl)-carbochlorination, the three-step process pathway for U_3O_8 reduction is: *step-1*, $2*U_3O_8 + 16*CO + 16*Cl_2 \longrightarrow 2*U_2Cl_{10} + 2*UCl_6 + 16*CO_2$; *step-2a*, $U_2CL_{10} + 5*H_2 \longrightarrow 2*U + 10*HCl$ and *step-2b*, $UCl_6 + 3*H_2 \longrightarrow U + 6*HCl$. ZEGOR® recycles HCl to Chlorine and water.

Twenty-nine samples of bauxites from different locations globally were analyzed for thorium and uranium by the noted geologists J. A. S. Adams and K. A. Richardson (see *Thorium, uranium and zirconium concentration in bauxite*, Dec. 1960 – attached). It has been established that primordial radionuclides thorium and uranium present in the world's bauxite deposits, concentrate at 5.73-fold and 5.33-fold their mean levels in the earth's crust, respectively. Parent isotopes are *inextricably-linked* to more than 30 radioactive decay progeny (from established nuclear physics) in bauxite and related mineral processing streams; and most decay progeny are gamma ray emitters (right: *Natural Decay Series* table, P. Metcalf for RSA's Council for Nuclear Safety).

A study of samples taken from alumina plants in Suriname and Arkansas (Adams-Richardson, ibid), determined that over 70% of parent thorium and uranium, and their decay progeny in Bayer digester output passes to red mud tailings. But decay chain progeny concentration in red mud tailings – due to ingrowth activity – continually increases in volume and radiotoxicity over time, as parent radionuclides decrease. In

Natural Decay Series

URANIUM - 238 DECAY SERIES			THORIUM - 232 DECAY SERIES			URANIUM - 235 DECAY SERIES		
NUCLIDE	DECAY	HALF LIFE	NUCLIDE	DECAY	HALF LIFE	NUCLIDE	DECAY	HALF LIFE
U - 238	ALPHA	4,5 E9 y	Th - 232	ALPHA	1,4 E10 y	U - 235	ALPHA*	7,1 E8 y
Th - 234	BETA*	24 d	Ra - 228	BETA	6,7 y	Th - 231	BETA*	24,6 h
Pa - 234	BETA*	1,17 m	Ac - 228	BETA*	6,13 h	Pa - 231	ALPHA*	3,43 E4 y
U - 234	ALPHA*	2,4 E5 y	Th - 228	ALPHA*	1,9 y	Ac - 227	ALPHA*	22 y
Th - 230	ALPHA*	8 E4 y	Ra - 224	ALPHA*	3,64 d	Fr - 223	BETA*	21 m
Ra - 226	ALPHA*	1,6 E3 y	Rn - 220	ALPHA*	55 s	Ra - 223	ALPHA*	11,2 d
Rn - 222	ALPHA*	3,8 d	Po - 216	ALPHA	0,15 s	Rn - 219	ALPHA*	3,92 s
Po - 218	ALPHA	3 m	Pb - 212	BETA*	10,64 h	Po - 215	ALPHA	1,8 E-3 s
Pb - 214	BETA*	26,8 m	Bi - 212	BETA*	60,6 m	Pb - 211	BETA*	36 m
Bi - 214	BETA*	19,7 m	Po - 212	ALPHA	304 E-9 s	Bi - 211	ALPHA*	2,16 m
Po - 214	ALPHA*	164 E-6 s	Pb - 208	STABLE		Tl - 207	BETA*	4,79 m
Pb - 210	BETA*	21 y				Pb - 207	STABLE	
Bi - 210	BETA	5 d						
Po - 210	ALPHA*	138 d						
Pb - 206	STABLE							

* DENOTES ACCOMPANYING GAMMA EMISSION

the case of bauxite washer plant tailings, concentrating decay progeny have likewise increased in volume and radiotoxicity over the decades. *In 1969, Logomerac found in Suriname red mud*, concentrations of niobium, germanium, zirconium, hafnium, uranium (no mention by him of either thorium or gallium), and extremely high levels of rare-earth elements such as lanthanum and yttrium as well as scandium (at 1700 ppm, 4.4-fold higher than in Jamaica). Later, in 1974, he reported similar concentrations in other bauxites.

Given conservation of mass, the greater portion of remaining radioactive impurities, say up to 20% of digester output, would ship with metallurgical BHH alumina to smelters, with up to 10% residual radioactive impurities going to alumina calciner emissions and in-plant scale accumulation in vessels and conduits. This implied Adams-Richardson empirical result conflicts with their other paper *Radioactivity of aluminum metal* that declares (more than estimated) 5% in shipped alumina, while drawing the industry-friendly conclusion that "… radioactivity of [BHH] aluminum is comparable with that of other common metals."

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[1] NORM: naturally occurring (primordial) radioactive materials with gamma-emitting decay progeny in mineral deposits.

The *Table 3: Bayer Process … impurities* (below right) shows a targeted alumina purity of 99.96% (from *SME Mineral Processing Handbook*) and impurities (in red) that include most of the original ore constituents, but <u>it is silent on radionuclides</u>, as is *Table 1* (below left, from the same SME Handbook) which shows the make-up of typical bauxite feedstocks around the world; note bauxite profiles for both Suriname and Jamaica.

Table 1. Typical Composition of Types of Commercial Bauxites

| Type | Gibbsitic, Massive | | | | Mixed Gibbsitic—Boehmitic | | | | Boehmitic Massive, Yugo-slavia, Istria | Diasporic Massive, Greece, Distomon district |
| | Arkansas, U.S.A. | | Suriname | | Earthy, Jamaica | | Pisolitic Massive | | | |
	Low silica	High silica	Moengo	Paranam	North Coast	South Coast	Australia Weipa	Guinea Boke		
Gibbsitic Al₂O₃	46.0	30.0	50.0	47.0	44.4	36.5	41.4	57.0		
Boehmitic Al₂O₃					2.8	8.2	12.0		ca 53.5	
Diasporic Al₂O₃										ca 58.0
Loss on ignition @ 1000°C	27.8	24.5	29.0	27.6	26.5	25.2	26.4	31.6	12.1	12.7
SiO₂, total	7.2	18.0	4.3	9.7	0.7	3.5	5.5	0.6	2.8	1.7
SiO₂, quartz					0.1	0.8	2.0		NR	NR
Al₂O₃, total	55.0	49.6	54.0	54.8	49.2	48.8	58.8	59.1	56.5	60.9
Fe₂O₃	6.0	4.7	8.8	4.3	19.3	19.5	6.8	5.1	24.2	20.4
TiO₂	2.0	1.6	2.7	2.3	2.5	2.5	2.3	3.3	3.3	2.9
CaO	0.1	0.04	0.01	0.03	0.06	0.17	<0.02	0.01	0.1	
MnO	0.15	0.15	0.01	0.01	0.80	0.27	0.005	0.02	0.07	
P₂O₅	0.2	0.1	0.06	0.1	0.40	0.21	0.10	0.07	0.8	
SO₃	0.6	0.5	0.6	0.6						0.02
Cr₂O₃	0.03	0.02	0.07	0.05	0.06	0.16	0.02	0.09	0.07	
CuO	0.00	0.00	0.00	0.00	0.01	0.004	0.02	0.01	0.004	
Ga₂O₃	0.01	0.01	0.01	0.01	0.01	0.01	0.005	0.01		
MgO					0.06	0.06	0.017		0.09	
NiO					0.07	0.03	0.005		<0.01	
PbO					0.01	0.01	<0.01		0.008	
V₂O₅					0.03	0.09	0.02		0.02	
ZnO	0.01	0.01	0.00	0.01	0.030	0.020	<0.002	0.01	<0.01	
ZrO₂	0.6	0.04	0.1	0.1	0.06	0.05	0.05	0.07		
Source: Ref. No.	4	4	4	4	5	5	5	4	5,6	6

Table 3. Bayer Process Reduction-Grade Alumina Impurities and Physical Properties—Range of Typical Values

Impurities, %		Impurities, %	
Si	0.004–0.010	Mn	0.0005–0.0015
Fe	0.009–0.030	Ti	0.001–0.005
Na	0.20–0.50	P	0.0005–0.001
Ca	0.01–0.07	Ga	0.01–0.05
Zn	0.005–0.015		

Physical Properties	Sandy Alumina	Floury Alumina
Loss on ignition, %	0.30–1.50	0.05–0.30
Alpha alumina, %	10–50	70–90+
Angle of repose, °	30–40	40–50
Sieve analysis, cum., %		
+100 mesh	1–10	0–5
+200 mesh	40–80	20–50
+325 mesh	85–98	50–70
Water sorption, %	1–3	0.2–0.5
Bulk density, lb per cu ft	55–60	50–60
Absolute density, g per ml	3.6–3.7	3.8–3.9+

Also Cu, Ni, Cr, B, K, Mg, Pb, etc., may be present at 0.0001–0.001% levels.
Source: Values taken from many sources.

Along with SME, the 1997 aluminum Industry-controlled study: *Managing Health in the Aluminum Industry* (MHIA, http://www.world-aluminium.org/media/filer_public/2013/01/15/fl0000116.pdf) skirts the issue of radioactive content with the carefully worded deception (see page 10): "… the NORM present in bauxite will concentrate in the Bayer process, and our investigations have shown that these elements partition to the bauxite residue rather than to alumina product." This amounts to saying there is no radioactive content in intermediate alumina, but recall the 1960 Adams-Richardson empirical results to the contrary had been published 37 years earlier, and almost certainly aluminum industry scientists knew of such pivotal findings. A shocking generalization in the MHAI study was clearly meant to deceive on this issue: "… the [human] body is unable to differentiate between stable and radioactive isotopes of the same element and that <u>as a consequence</u> they [the isotopes] behave identically in the body" (page 121). After suppressing the fact of significant radioactive impurities, including radon, in shipped alumina, the MHAI is also silent on highly radiotoxic radon in human neurological disorders (see following page).

Yet another industry-controlled report was issued April 2013: *Bauxite Residue Management: Best Practice*.

Like the MHIA, the BRM_BP report is equally silent on radioactive decay progeny in bauxite and the mineral processing stream. The report makes a mere mention of the word "series" without elaborating on the 30+ decay progeny occurring in the three main decay series (above: *Natural Decay Series* table, P. Metcalf for RSA's Council for Nuclear Safety). This BRM_BP report claims a <u>high-end</u> thorium-in-bauxite ratio of 5.73-fold increase over crust. This value equals our <u>mean</u> ratio which is based on the December 1960 Adams-Richardson empirical results). BRM_BP seems to counter EPA and Adams-Richardson published positions by indicating <u>no</u> radioactive content in alumina.

Bauxite Residue Management: Best Practice

April 2013

WORLD ALUMINIUM

european aluminium association

Research links Alzheimer's to radon

Source: Fix-Your-Radon.com

In a study conducted at the University of North Dakota, researchers discovered that the concentrations of radioactive radon daughters in the brains of non-smoking persons with Alzheimer's and Parkinson's disease averaged about 10 times greater than in the brains of persons with no previous evidence of neurological disorders. Professor Glenn Lykken and Dr. Berislav Momcilovic assert their study demonstrates that indoor radon gas has the capacity to irreversibly infest the brain with the poisonous progeny of radioactive heavy metals.

Recently revised EPA risks assessments estimate 21,000 Americans die annually from radon induced lung cancer, 150% higher than their 1994 estimate. However, scientists are increasingly suspicious that radon may be linked to disease in other parts of the body as well.

When inhaled, radon gas accumulates in lipid tissue throughout the body with the highest concentration in the brain, bone marrow, and nervous system. Additionally, one-third of the inhaled radon decay products (radioactive particles produced when the gas decays) pass from the lungs into the blood stream indicating that the gas does not flow quickly in and out of the lungs, but lingers in the body.

Previous studies at UND determined that radon is rapidly absorbed into the body through the lungs, it accumulates in the cranium resulting in increased gamma ray emissions from bismuth-214 (one of the radioactive radon decay products) and altered EEG signals.

While radon is a lipid-soluble gas that can move freely in and out of the brain despite the blood-brain barrier, none of the transmuted heavy metal radon daughters are soluble in the lipids, meaning they remain trapped in the brain where they emit gamma radiation and alpha particles resulting in both radiation and chemical injury to the brain cells.

Of keen interest was the unexpected discovery that the radioactivity selectively accrues to the brain proteins in the Alzheimer's victims and to the brain lipids in the Parkinson's victims. This pathognomonic distribution was inferred to reflect the increase of local chlorine availability to which the radon daughters bound selectively.

Once present, the most likely candidate for radiation injury appears to be the highly radiosensitive astrocytes rather than the more radio-resistant neurons, which do not divide. Other studies have indicated the astrocytes may be involved in Alzheimer's disease and the amyloid deposits and neurofibrillatory tangling observed with Alzheimer's may well reflect the response to radiation injury of the astrocytes.

An estimated 4.5 million Americans have Alzheimer's disease, the number having doubled in the last 25 years. An estimated 1.5 million Americans have Parkinson's disease with 60,000 new cases diagnosed each year.

Radon mitigation not only protects health, it also helps to keep basements dry and air conditioning costs low by greatly reducing entry of water vapor from the soil.

Interestingly enough, the geographic distribution of Parkinson's disease mortality is considerably higher in states with a greater radon potential, according to research by D.J. Lansak of the University of Kentucky and published in the Journal of Neurological Sciences.

Not just Western aluminum has been silent on the presence of NORM in bauxite and TENORM[3] in the BHH mineral processing stream. In the late 1970s Aluterv-FKI, an agency of Hungary – then a USSR state – was contracted to conduct a process study (including gallium recovery) for the Linden Guyana bauxite complex. The study included a characterization of minerals in the processing stream, but as shown in adjacent Aluterv-FKI table, it excluded mention of TENORM as did the foregoing tables of the *SME Mineral Processing Handbook* and MHIA. However, Hungarian and Yugoslavian researchers [Kiss, J (1952), Mehes, K (1951) and Ristic (1956)] had already reported on radioactivity in the bauxites of those countries. Consequently, Aluterv-FKI already had institutional knowledge of radionuclides in bauxite and should have reported it for Linden.

ALUTERV-FKI Chemical Composition of Bauxite/MAZ, laterite, sand and red mud

	A	B	C	R	S	R.M.	K
L.O.I.	28.6	28.7	22.3	28.4	14.0	7.9	27.5
Fe_2O_3	3.5	2.0	33.3	8.0	34.5	12.7	18.7
Al_2O_3	55.3	55.8	38.4	53.3	25.9	26.7	47.4
SiO_2	8.2	9.2	2.7	6.4	18.6	22.2	3.4
TiO_2	2.8	2.9	2.8	2.7	2.7	11.7	2.6
FeO	0.3	0.4	0.4	0.6	1.2	N.D.	3.6
P_2O_5	0.10	0.09	0.09	0.09	N.D.	0.30	N.M.
V_2O_5	0.06	0.03	0.18	0.07	0.16	0.20	N.M.
MnO_2	0.02	< 0.01	0.03	0.02	N.M.	N.M.	N.M.
CaO	0.1	0.1	0.1	0.1	N.M.	0.8	N.M.
MgO	0.05	0.03	0.03	0.04	N.M.	0.05	N.M.
SO_3	0.74	1.10	0.49	0.77	1.2	N.M.	N.M.
Ga_2O_3	0.005	0.005	0.003	0.005	0.005	0.003	N.M.
$C_{org.}$	0.153	0.182	0.460	0.164	0.170	0.177	N.M.
Na_2O	N.M.	N.M.	N.M.	N.M.	2.5	13.8	N.M.

Column headers: A & B: MAZ samples; C: laterite; R: poidomitor sample; R.M.: red mud; S: Sand classifer discharge; K: Kara Kara bauxite

N.M.: not measured; N.D.: not detectable

Radionuclides and decay progeny in the BHH smelter pot According to *Perturbation of Nuclear Decay Rates*, by G. T. Emery, (see attached Perturb-Decay Rates 1972), analysis has shown that "decay rates … of NORM are … unaffected by external conditions such as high temperature, pressure, the chemical environ-ment, and electric, magnetic, or gravitational fields as encountered by primordial radionuclides in stellar interiors" or on earth in the smelting pot producing BHH aluminum. Consequently, radionuclides contained in BHH alumina input to a smelter passes through unaffected by the high heat and chemistry in the smelting pot into finished aluminum metal. Moreover, there is yet another **deception that radionuclides are vaporized** by the high temperature (980°C) of the Hall alumina smelter pot, but this claim is readily countered by boiling-point data on radionuclides and their oxides being well above mean Hall smelting temperature and so cannot vaporize as suggested. This is also applicable to the question of smelter radionuclide vaporization for copper which has a mean pot temperature of 1,085°C. Here boiling points for key radionuclides are too high and so cannot vaporize.

Radiological dosage protocol To be viable, the notion of acceptable radiological dosage in BHH aluminum of parent radionuclides U-238 and Th-232 measured at an instant in time, against pre-determined standards of exposure, must also take into account the post-smelter radionuclide progeny ingrowth in finished aluminum/ alloys, since many of these progeny <u>are more radiotoxic than their parents</u>.

Specifically, the post-smelter formation of lead-210, radium and radon that, in turn, decays to radiotoxic isotopes like bismuth-212 and -214, and increased release of gamma radiation, must be included. With the aluminum industry being silent on the presence of more than 30 decay progeny in metallurgical alumina and BHH aluminum and excluding related quantification factors from dosage computations, accurate dosage levels have not been reliably determined by the industry. Despite the silence of the aluminum industry on radioactive decay progeny, even though they are inextricably linked to primordial parent radionuclides in bauxite/laterite, some scientists are researching and publishing on the subject. The explicit mention and detailed discussion of [26]Al and ^{67}Ga in MHAI is now seen as a distraction from the far more extensive and radiotoxic natural decay progeny and the passage of these radionuclides into shipped alumina and aluminum end-products. However, even though minor, the radioisotopes

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[3] TENORM: Technologically-enhanced naturally occurring radioactive materials

^{26}Al (boiling point=2,467°C; half-life=717,000 years) and ^{67}Ga (boiling point= 2,403°C; half-life=3.3 days) are continually produced in their respective decay chains as long as their parents exist. These two decay progeny do pass through alumina into aluminum without smelter evaporation given their high boiling points. As depicted in the adjacent flowcharts, the decay chains of radionuclides phosphorus-26 (for ^{26}Al) and bromine-68 (for ^{67}Ga) that exist in bauxite/laterite terminate on the stable isotopes of ^{26}Mg and ^{67}Zn.

Felix Padel (Charles Darwin's great-great-grand-son) teamed with an Indian journalist to discuss a 2010 break in a red mud pond dike in Hungary and its implications for new Bayer refineries starting up or being erected in Indian (2010). Regarding radioactive content in the red mud they wrote: "Bauxite is formed in alternating seasons of rain and sun over millions of years that leaches out some minerals and keeps others including at least 22 radioactive elements. Strange this has **not been highlighted in news** of the Hungarian disaster!" Padel also stated: "… Jamaica and Australia, two of the world's largest bauxite-alumina producers, both banned early attempts to make bricks out of red mud, since red mud is toxic not just from dangerously corrosive caustic soda; it is also radioactive." A review of the natural decay series table above reveals the many radioisotopes found in bauxite/laterite, even greater than the 22 mentioned in Padel's article.
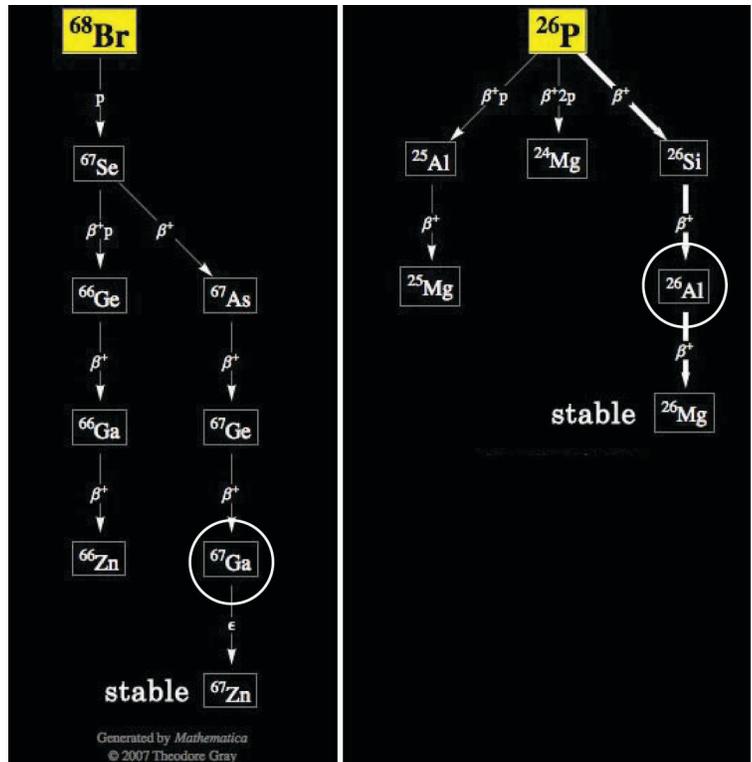
http://www.savingiceland.org/2011/04/people-can%E2%80%99t-be-made-to-bathe-in-red-mud/

Thorium, uranium and zirconium concentrations in bauxite

Abstract: Twenty-nine samples of bauxites from different locations were analyzed for Th and U by gamma-ray spectrometric, alpha counting, and wet chemical methods. The Th concentrations range from 5.0 to 131 ppm and average 48.9 ppm [63]. The U concentrations range from 2.7 to 26.7 ppm and average 11.4 ppm [12]. The Th-to-U ratios range from 1.5 to 20.9, with an average value of 5.1. Zr determinations on some of the bauxites gave values ranging from 0.02 to 0.65% Zr, and averaging 0.09% Zr. The Th, U, and Zr contents of the bauxites are related to the type of source rock. A study of samples from alumina plants treating Surinam and Arkansas bauxites shows that during the process, over 70% of the Th and U in these 2 bauxites is concentrated into the red mud, and the alumina contains very small amounts of these elements. This study also indicated that much of the Th and U in bauxites occur in either primary or secondary resistate minerals. *See attached full article.*

Radioactivity of aluminum metal

Abstract: Although Al is produced from bauxite containing 74 ppm of Th and 3.6 ppm of U, less than 5% of these amounts is extracted with the alumina in processing. The radioactivity of Al is comparable with that of other common metals. *See attached full article.*

Cleansing the mineral processing stream of naturally occurring radioactive materials (NORM)

This aspect of the ZEGOR® Process was prompted by repeated accounts of radiation-like illness and deaths in an old South American bauxite mining/mineral processing community and its overseas Diaspora. While primordial parent radionuclides of thorium and uranium have decay half-lives in the billions of years, the half-lives of carcinogenic radon gas and its decay progeny range from seconds to a few days. Even as a minor trace, radon rapidly decays to solid isotopes of lead, bismuth, polonium and other toxic daughters that release gamma radiation in humans, causing neurological disorders and cancers of bone, breast and lymph glands.

The need for cleansing such feedstock is further emphasized by the adjacent mineral map of the African **DRC-Zambia copper belt**. This map depicts well the variety and extent of valuable metallic ores – found there and across Southern Africa – that are NORM laced. While there are copper, gold and uranium deposits in the Guiana Shield and NORM in its bauxite/laterite, little mention is made of radioactive minerals that include these stable elements, as is reported elsewhere. As indicated in a 2012 paper: *Mineralogical and geochemical studies of boron-rich bauxite ore … in Songqi, SW Henan, China*. Chinese geologists used standard analytical apparatus to determine mineralogical and chemical composition of bauxite samples; the published data (their table 1) show the occurrence of primordial radionuclides and, by implication, decay progeny in bauxite. This recent study confirms the 1960s' findings of then noted U.S. geologists Adams and Richardson on radionuclides in bauxite, suggesting such standard analytical apparatus could have, and may have, been used earlier by the global aluminium industry to determine radioactive content in bauxite. To reiterate, we contend ZEGOR® will achieve radioactive cleansing of bauxite ores through its improved carbochlorination/MFBR separation and purification steps.
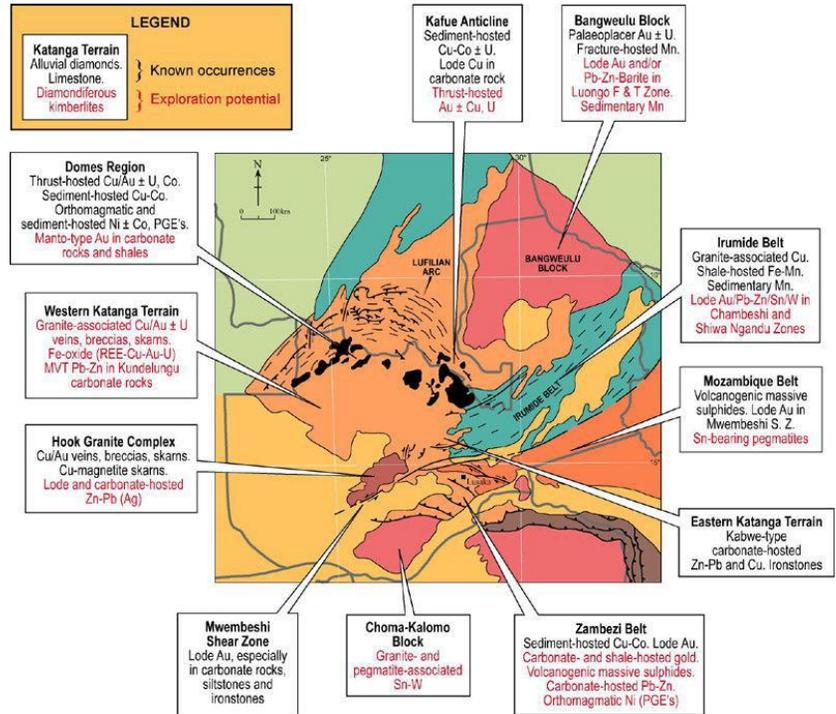
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THORIUM, URANIUM AND ZIRCONIUM CONCENTRATIONS IN BAUXITE [1]

J. A. S. ADAMS AND K. A. RICHARDSON

CONTENTS

ABSTRACT

Twenty-nine samples of bauxites from different locations were analyzed for thorium and uranium by gamma-ray spectrometric, alpha counting, and wet chemical methods. The thorium concentrations range from 5.0 to 131 ppm and average 48.9 ppm. The uranium concentrations range from 2.7 to 26.7 ppm and average 11.4 ppm. The thorium-to-uranium ratios range from 1.5 to 20.9, with an average value of 5.1. Zirconium determinations on some of the bauxites gave values ranging from 0.02 to 0.65 percent Zr, and averaging 0.09 percent Zr.

The thorium, uranium and zirconium contents of the bauxites are related to the type of source rock. Bauxites derived from nepheline syenites contain more thorium and uranium than bauxites derived from other rock types; bauxites derived from basic igneous rocks have the lowest thorium and uranium concentrations, and bauxites derived from carbonate rocks have the lowest thorium-to-uranium ratios. The greatest concentrations of Zr were found in bauxites derived from nepheline syenites, and bauxites derived from carbonates contained the lowest concentrations of Zr.

A study of samples from alumina plants treating Surinam and Arkansas bauxites shows that during the process, over 70 percent of the thorium and uranium in these two bauxites is concentrated into the red mud, and the alumina contains very small amounts of these elements.

This study also indicated that much of the thorium and uranium in bauxites occurs in either primary or secondary resistate minerals.

INTRODUCTION

FOR some time it has been known that certain bauxites contain greater amounts of thorium and uranium than the average crustal rocks. The primary purpose of this study was to make a general survey of bauxites to investigate the distribution of radioactive elements, and determine the significance of this distribution.

In addition to contributing to the geochemical knowledge of thorium and uranium, the results of this study may have some economic value. The possibility of by-product recovery of thorium is suggested, also the possible use of radiometry in prospecting for aluminum ore.

PREVIOUS WORK

Although no data regarding the absolute thorium and uranium contents of bauxites have been found in the literature, with the exception of recently published papers by Adams and others, there are a number of papers that give theoretical reasons to expect relatively high concentrations of these elements in bauxites, and a number of qualitative reports that support the theory.

The application of the concept of ionic potential to the behavior of elements during weathering has been discussed by Goldschmidt and, with particular reference to Arkansas bauxite, by Gordon and Murata. The latter paper verifies Goldschmidt's statement regarding the effect of bauxite formation on certain elements, showing beryllium, chromium, copper, gallium, lead, manganese, molybdenum, niobium, scandium, titanium, vanadium, yttrium and zirconium to be concentrated, and barium, calcium, lanthanum, magnesium and strontium to be depleted during the alteration of nepheline syenite to bauxite.

Figure 1 is a plot of the ionic radius against the ionic charge for a number of elements. Values for the ionic radii are taken from Ahrens. The diagonal lines on the figure are the lines of equal ionic potential used by Goldschmidt, and Gordon and Murata as the boundaries for the group of elements with intermediate ionic potential values that are precipitated in nature as hydrolyzates. Tetravalent thorium and uranium lie well within these boundaries; hexavalent uranium is near the field of elements which form soluble complex anions.

From consideration of the ionic potential alone, thorium should be concentrated in bauxites, whereas uranium might be oxidized and removed as the soluble uranyl ion, UO_2^{++}. Measuring the radioactivity of Arkansas bauxite by beta counting, Frederickson found an equivalent radium content of 13.1×10^{-12} grams/gram of bauxite. This is larger by approximately one order of magnitude than the average value for acid igneous rocks. Frederickson believed that uranium was introduced into the deposit as uranyl ions and concentrated by adsorption on the aluminum minerals.

Similarly, Lovering concludes from investigations of radioactive iron oxides that "colloidal ferric oxide hydrate" adsorbs uranyl ion, and thus removes uranium from solution. Most of the thorium minerals resist weathering and remain in their original form, but tetravalent thorium would also be removed from solution by ferric hydroxide. During crystallization of the ferric colloid adsorbed uranium is expelled and forms separate minerals. Heinrich discusses radioactive gossans and laterites briefly, agreeing with Lovering's conclusions.

Davidson states that some terra rossa deposits in Central Africa are significantly radioactive. The radioactive elements are again reportedly adsorbed on the iron hydroxides, but in contrast to the above authors, David-
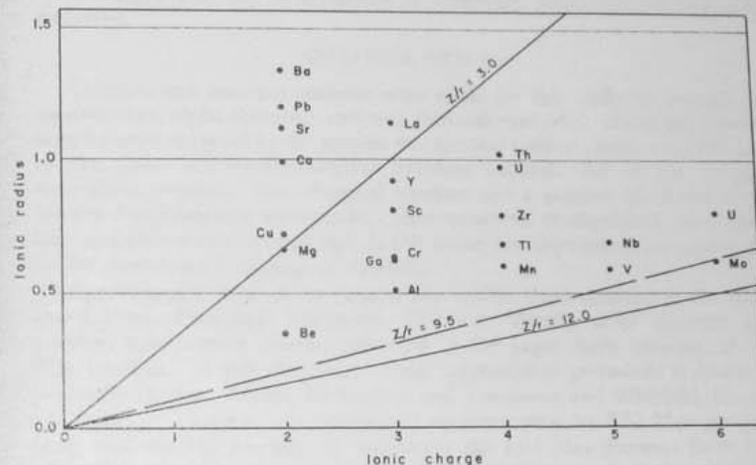

Figure 1.   Grouping of certain elements according to ionic potential.

son believes that the parent uranium is largely leached and the radioactivity is due to thorium series and uranium series daughter elements.

Kiss and Mehes have studied Hungarian bauxites and reported their radioactivity. Using nuclear emulsions, Kiss detected a small amount of radioactivity in tabular inclusions within zircon crystals. Mehes, measuring radioactivity in the field, found a relationship between radioactivity and ore grade, with increased radioactivity also along lines of faulting and folding in the bauxite.

Occurrences of bauxites with uranium have been found in Yugoslavia, according to Ristic, which ". . . will apparently also become a source for the obtaining of uranium, because in the processing of aluminum, the uranium concentrates itself in the so-called red mud."

SAMPLES STUDIED

Samples of 29 bauxites (Table I) from different countries were analyzed for this study. It is thought that they constitute a fairly representative collection. Among the samples are bauxites derived from both acid and basic igneous rocks, metamorphic, clastic and carbonate sediments. Parent rocks of Irish and Jamaican bauxites were also analyzed. Table I lists the samples, giving their geographic location, known or inferred parent rock, and literature references.

Table I. List of Bauxite Samples

Sample	Location	Parent Rock	Reference
KR-1	French Guinea	nepheline syenite	Fermor (1915)
KR-2L	Gold Coast	volcanic ash	Cooper (1936)
KR-3 KR-3B	Dominican Republic	limestone	Goldich and Bergquist (1947)
KR-4 KR-4B KR-5L	Jamaica " "	White limestone	Hartman (1955) Hill (1955)
KR-6L	Brazil	nepheline syenite	Teixeira (1942)
		Other parent rock types for Brazilian bauxites, reported in Fischer's (1955) bibliography, are: granite (Knecht), gneiss (Froes), schists (Goodchild) and phyllite (Guimaraes).	
KR-7L	British Guiana	diabase	Kersen (1955) Harrison (1910)
KR-8L	India	basalt	Fox (1923)
KR-9L	Bintan, East Indies	hornfels	Bemmelen (1941, 1949)
KR-10	Palau Islands	tertiary volcanics	Bridge and Goldich (1948)
KR-11L	Istria, Yugoslavia	mesozoic limestone	U.S. Bureau of Mines (1953)
KR-12L	Dalmatia, Yugoslavia	mesozoic limestone	Franotovic (1955)
KR-13L	Italy		Harder (1949)
KR-14L	France	mesozoic limestone	Lapparent (1949)
KR-15L	Greece	mesozoic limestone	Frantovic (1955)
KR-17L KR-18	Henry, Georgia Georgia	kaolinite	White and Benson (1952)
KR-20L	Oregon	miocene basalt	Allen (1948); Libbey, Lowry and Mason (1946)
KR-22	Mississippi	Porters Creek shale	Burchard (1924); Morse and Hand (1923)
KR-23L	Missouri	palaeozoic limestone	Keller (1944)
KR-26 KR-31	Surinam Surinam	igneous and metamorphic	Kersen (1955) Meulen (1949)
KR-27 KR-38	Arkansas Arkansas	nepheline syenite	Mead (1915)
KR-80 KR-83	Jamaica Jamaica	White limestone	(see KR-4, above)
KR-84	Antrim, Northern Ireland	basalt	Eyles (1952)

In addition to the individual bauxite samples, a suite collected on the Aluminum Company of America property at Bauxite, Arkansas, illustrates some of the types of bauxite deposits and stages in the development of bauxite from the nepheline syenite parent rock. A section of drill core from the same area, extending through the bauxite into the top of the syenite, was also studied.

To trace the radioactive elements through the processing of bauxite to alumina, material balance samples from two treatment plants were studied. These samples consisted of the feed bauxite, calcined alumina, red mud, and coarse sand, from plants operating on Surinam bauxite and on Arkansas bauxite.

The alpha activities of a number of aluminum metal samples were also measured.

ANALYTICAL METHODS

Thorium and uranium analyses were made for this study by gamma ray spectrometry, alpha counting, and wet chemical methods. All of the bauxite samples were analyzed by the gamma ray spectral method; some were checked by the alpha activity-fluorometric uranium method. All of the samples were alpha counted. One chemical thorium and a number of chemical zirconium determinations were made. Determinations of aluminum, iron, titanium, and silicon oxides presented in this paper are the routine analyses made by the Aluminum Company of America.

Approximately half of the gamma ray results were obtained at the Shell Development Company laboratory, Houston, Texas; other thorium and uranium spectrometer results presented in the paper were obtained at the Rice Institute. A full discussion of the spectrometry procedure is found in papers by Hurley; Adams, Richardson and Templeton and Whitfield, Rogers and Adams. Thorium was determined by measuring the 2.62 Mev gammas from thallium-208, uranium by measuring the 1.76 Mev gammas from bismuth-214, and thorium and uranium concentrations were both calculated from counts made on a channel centered at 0.61 Mev. Potassium was determined for some samples, using the 1.47 Mev gammas given off by potassium-40. Potassium content of bauxite is low, but the measurements were conveniently obtained, and are therefore included (Table IX).

Individual limits of error for the gamma ray spectral values are not given. The number of events recorded for each measurement was sufficient to give a statistical error of less than ± 5 percent. Additional sources of inaccuracy are the "physical errors" inherent in this method, and the possible inhomogeneity of the samples. A result of the very high thorium concentration in bauxites is the smaller error in thorium measurements. Ninety percent of the chemical thorium analyses made by Pliler agree to within 10 percent with the gamma ray measurements. However, the accuracy of the uranium measurement suffers from the increased thorium contribution to counts made at 1.76 Mev. Uranium measurements are judged accurate to well within ± 20 percent, the greatest inaccuracy being in samples with high thorium-

to-uranium (Th/U) ratios. Potassium measurements are considered to be accurate to within ± 5 percent of the amount present.

Calculation of thorium and uranium concentrations from thallium-208 and bismuth-214 gamma activity is based on the assumption that the thorium and uranium decay series are in secular radioactive equilibrium. Determinations of thorium and uranium by two independent methods showed samples of Arkansas and Surinam bauxites to be in equilibrium, but the fluorometric uranium procedure does not apply well to bauxites, due to (i) the difficulty in extracting all of the uranium from the sample, and (ii) interference of the high iron content of many bauxites with the fluorescence. However, a
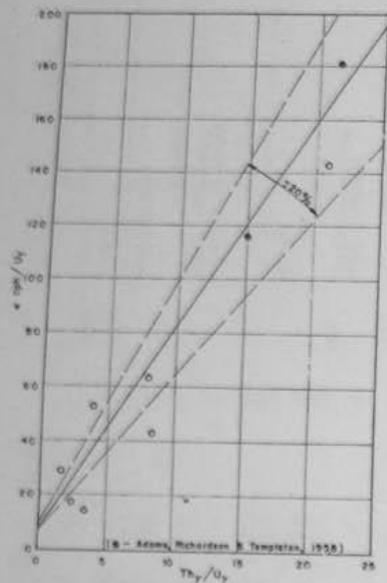

Figure 2.   • cph/U_f versus Th_γ/U_γ

Figure 3.   Th and U data on bauxites.

few samples were analyzed by this method and the data obtained (Table II) are shown in Figure 2, a plot of (alpha counts per hour/fluorometric uranium) against the gamma ray thorium-to-uranium (Th/U) ratio.

Figure 2 contains too few data to lend itself to a definite interpretation, but it appears that the relationship

$$\frac{\text{alpha cph}}{U_f} = K_1 + K_2\left(\frac{Th_\gamma}{U_\gamma}\right)$$

for bauxites may have a smaller K_2 value than that determined by Adams, Richardson and Templeton for a group of sediments composed predominantly
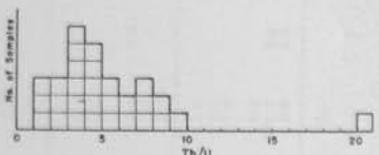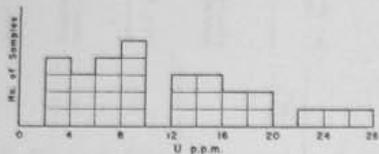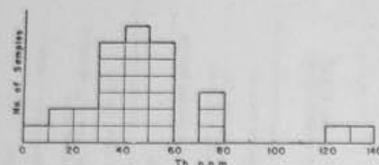
of limestones and shales. The diagonal line drawn on Figure 2 is taken from Adams et al. and represents the above relationship with values of 7.80 and 7.57 for K_1 and K_2, respectively.

The departure of the fluorometrically determined uranium values from the gamma ray values for samples KR-10, KR-38 and KR-80 might be attributed to lack of sample homogeneity, to absence of radioactive equilibrium, or, for samples KR-10 and KR-38, to incomplete extraction of the uranium in the chemical analysis. Because the thorium and uranium in a number of bauxites have been shown to be in equilibrium with their daughter elements, this paper continues on the assumption that this condition exists for all of the bauxites studied.

RESULTS AND DISCUSSION

Distribution of Thorium and Uranium in Bauxites.—The thorium and uranium analyses of 29 bauxite samples are given in Table II. The bauxites are divided into four groups on the basis of the type of rock from which they were derived; the parent rock types are acid igneous, basic igneous, shale, and limestone. Average thorium and uranium contents for each of the bauxite groups are shown in Table III, with averages for the parent materials taken from the literature.

In some cases there is doubt regarding the exact type of rock from which the bauxite is derived. The location of the Brazilian sample, for instance, is known only by the country. This bauxite may be derived from any of a number of acidic or metamorphic rocks (Table I), depending on which specific deposit was its source. The parents of other South American samples are also questionable. Discussions by Goldich and Bergquist and Hill indicate some uncertainty regarding a purely limestone parent rock for the Caribbean ores.

In grouping the bauxite samples the following relationships were considered: (i) the Caribbean and European bauxites, and the Missouri diaspore clay have limestone parent rocks; (ii) the Georgia and Mississippi samples are derived from shales, and included with them is the Bintan sample whose parent is a low grade metamorphic hornfels; (iii) basic igneous rocks are the parents of the bauxite samples from the Gold Coast, British Guiana, India, Palau Islands, Oregon, U.S.A., and Antrim, Ireland; (iv) acid igneous rocks, mainly nepheline syenites, are parents of the samples from French Guinea, Brazil, Surinam and Arkansas, U.S.A.

It is evident from the data in Tables II and III, not only that the thorium and uranium contents of bauxites are generally much greater than the average for crustal rocks, but also that there is a definite relationship between the thorium and uranium contents of a bauxite and its parent rock type.

For the 29 bauxite samples the thorium concentration ranges from 5.0 to 131. ppm and has an average value of 48.9 ppm; the uranium ranges from 2.7 to 26.7 ppm and has an average value of 11.4 ppm. The Th/U ratio ranges from 1.5 to 20.9 with an average value of 5.1 (Fig. 3).

The higher concentration of thorium and uranium in acid igneous rocks

Table II. Thorium and Uranium Determinations on Bauxites

Parent Rock	Sample	ppm Th	ppm U	Th/U	U α ppm	α cpm*	α cpm* / U
Carbonate	KR-3	34.5	9.6	3.3		285	
	KR-23	34.8	8.1	4.3		194	
	KR-4	43.7	18.6	2.3	17.5	306	17.5
	KR-49	42.0	17.0	2.5		164	
	KR-55	46.5	26.7	1.7		336	
	KR-111	47.3	6.5	7.3		365	
	KR-126	43.8	8.4	5.2		242	
	KR-131	31.5	8.3	6.2		280	
	KR-144	55.6	12.4	4.5		265	
Shale	KR-151	39.2	7.3	7.9		306	
	KR-231	56.0	13.0	4.3		361	
	KR-50	32.1	9.5	3.4	17.7	255	14.4
	KR-63	39.4	23.4	1.7	7.1	407	
Basic Igneous	KR-94	58.7	7.1	8.3		305	
	KR-171	46.6	13.5	3.5		321	
	KR-18	34.6	15.4	2.2		239	43.0
	KR-22	36.3	5.9	6.2	5.9	179	
	KR-2L	21.2	2.7	7.9		176	
	KR-7L	40.2	5.0	8.0	2.9	247	60.7
	KR-8L	23.2	6.5	3.6		215	
Acid Igneous	KR-10	5.0	3.3	1.5		12	
	KR-20L	19.3	4.5	4.3	0.4	138	30.0
	KR-24	15.1	2.9	5.2		114	
	KR-1	127.4	24.1	5.3		1253	
	KR-6L	34.3	15.7	3.5		419	
	KR-26	72.0	17.0	4.2		530	
	KR-27	130.7	14.4	9.1	3.1	405	142.6
	KR-31	74.2	3.6	20.6	6.6	442	52.7
	KR-38	75.8	19.8	3.8		348	
Average (29 samples)		48.9	11.4	5.1			

* For sample surface of 20.3 cm²

Table III. Average Values for Thorium, Uranium and Th/U Ration in Bauxites and Parent Rocks

Rock Type	ppm Th	ppm U	Th/U
Carbonate rocks*	1.1	1.3	0.9
Concentration factor	(40.8)	(9.9)	(4.7)
Bauxites derived from carbonates (13 samples)	44.9	12.9	4.2
Uranium leached		(76%)	
Shales*	12.0	3.7	3.8
Concentration factor	(3.7)	(2.8)	(1.3)
Bauxites derived from shales (4 samples)	44.1	10.5	5.1
Uranium leached	(23%)		
Basic Igneous*	3.9	0.96	4.0
Concentration factor	(5.3)	(4.4)	(1.2)
Bauxites derived from basic igneous rocks (6 samples)	20.7	4.2	5.2
Uranium leached		(18%)	
Acid Igneous*	13.0	3.0	5.0
Concentration factor	(6.9)	(5.3)	(1.6)
Bauxites derived from acid igneous rocks (6 samples)	89.1	15.8	7.8
Uranium leached		(24%)	

* Evans and Goodman (1941)
** Adams and Weaver (1958)

as compared with basic igneous rocks is reflected by the bauxites derived from them. The bauxites with acidic parents are approximately four times richer in these elements than bauxites with basic parents. Bauxites derived from shales and carbonates are quite similar in both thorium and uranium content and are intermediate between the other two groups. The comparable radioactivities of the shale and limestone derivatives is not surprising if one considers, as Hartman suggested for Jamaican bauxite, that the source of the residual lateritic material is the clay impurity in the limestone.

It is noted from the data in Table II that the group of bauxites derived from carbonate rocks has the lowest Th/U ratio, and those derived from acid igneous rocks have the highest ratio. The low ratio for bauxites with limestone parent rocks is particularly well exhibited by the Caribbean samples, none of whose Th/U ratios is greater than 4.3.

Shown in Table III are average concentration factors for thorium and uranium during the formation of bauxite from the various types of source rock. The magnitude of these factors is dependent on two quantities: the fraction of the original rock mass removed in solution, and the amount of thorium and uranium leached. Assuming the thorium remains fixed, then the minimum concentration factor for this element depends only on the amount of parent rock removed. In the alteration of limestone to bauxite the thorium concentration is greatest, averaging 40-fold, while the alteration of shale results in less than 4-fold concentration of the thorium. As pointed out by Adams and Weaver, if all the thorium and uranium occurred in resistate minerals, lateritic weathering would concentrate both elements without changing the Th/U ratio. For each of the four groups of bauxites, the ratio is higher than the average for the parent rock type. Using the assumption that no thorium is lost, the concentration factor for this element multiplied by the uranium concentration of the parent rock gives the uranium concentration that the bauxite would have if no uranium were removed during bauxite formation. From such calculations it is estimated that approximately 20 percent of the uranium is leached from the igneous and shale parent rocks, and 75 percent from the carbonate rocks during lateritization. This is in close agreement with Adams and Weaver's report that an average of 80 percent of the uranium in a carbonate rock can be brought into solution by dissolving in weak acid.

From the foregoing considerations, and the rather general data in Table III, the following conclusions are drawn. In bauxites whose parent rocks are carbonates, the uranium retained is only the portion that occurred in the resistant minerals of the carbonate rock. Such a conclusion may also be valid for bauxites derived from shales and igneous rocks, in which case 70 to 80 percent of the uranium in shales and igneous rocks may occur either in primary or secondary resistate minerals. Because the Th/U ratio increases during bauxite formation, perhaps more of the thorium than of the uranium occurs in primary or secondary resistate minerals.

The reliability of the assumption that thorium is relatively immobile is demonstrated by the low Th/U ratio found in stream and ocean waters. Adams, Osmond and Rogers give a value of less than 0.01 for this ratio.

Table IV. Thorium and Uranium Contents of Some Bauxites and Their Parent Rocks

Sample	Location	ppm Th	ppm U	Th/U
KR-55, Nepheline syenite	Bauxite, Arkansas (Drill Core Samples)	19.3	4.9	3.9
Average of 5 bauxites		52.0	6.2	8.4
KR-81, limestone	Jamaica	(~0.2)*	1.3	<0.2
KR-80, bauxite		12.1	9.5	3.4
KR-88, basalt	Antrim, N. Ireland	(~0.5)*	(<0.2)*	(4.0)**
KR-84, bauxite		15.1	2.9	5.2

* Error approaches 100% for such low level measurements
** Probable value (see Adams, Osmond, Rogers, 1959)

Table V. Thorium and Uranium in Arkansas Bauxite and Nepheline Syenite Samples

Location	Sample	Description	ppm Th	ppm U	Th/U
Section 17	KR-54	Top of transported bauxite deposit	65.9	15.7	4.2
Section 16	KR-55	Fresh nepheline syenite	19.3	4.9	3.7
	KR-56	Weathered nepheline syenite	45.9	9.4	4.9
	KR-59	Limonite band between KR-56 and KR-57	36.9	2.3	16.1
	KR-57	Weathered, kaolinitic syenite	49.4	10.9	4.6
	KR-60	Clay layer between weathered syenite and bauxite	33.9	7.9	4.3
	KR-58	Near bottom of bauxite (pisolitic)	51.8	3.5	14.8
	KR-62	10 ft. horizontally from KR-58	34.0	10.3	3.3
	KR-63	10 ft. horizontally from KR-62	57.1	6.5	8.8
	KR-61$_1$	Near top of bauxite, 7 ft. above KR-58	90.5	3.9	13.0
	KR-61$_2$	Same horizon as KR-61$_1$	66.8	7.0	9.6
Section 26	KR-64	Granitic textured bauxite	77.5	24.9	3.1
	KR-65	Clay veinlets in bauxite	36.9	4.4	8.4
	KR-66	Pisolitic bauxite overlying KR-64	106.3	21.4	5.0

* Township 2 South, Range 14 West, Saline County, Arkansas

Comparison of the Thorium and Uranium Contents of some Bauxites with their Parent Rocks.—Table IV gives thorium and uranium data for bauxite samples from Arkansas, Jamaica and Northern Ireland, and for samples of their parent rocks, nepheline syenite, limestone and basalt, respectively, taken from the same areas as the bauxite samples. The Arkansas samples are taken from a drill core discussed in detail below. The nepheline syenite sample is somewhat kaolinized. The samples of Jamaican and Irish parent rocks are fresh.

Regarding the Arkansas samples in Table IV, the nepheline syenite is rather richer in thorium and uranium than the average acid igneous rocks; the bauxite contains less than the average amounts given in Table III for similar bauxites. The actual thorium and uranium concentrations of individual samples may not be highly significant, for it is shown later that the concentrations vary considerably within this deposit. Furthermore, the nepheline syenite, KR-55, is not quite fresh, and its thorium and uranium concentrations and the Th/U ratio may be greater than the unaltered rock.

The Jamaican parent rock contains an average amount of uranium for a limestone, but very little thorium. The typically low Th/U ratio of the limestone is reflected by the low ratio, 3.4, in the bauxite, KR-80. The thorium and uranium concentrations in KR-80 are close to the averages in Table III. Hartman estimated that 667 tons of the White limestone would be required to produce one ton of bauxite of 50 percent Al_2O_3. Using this estimate, and assuming no thorium is lost during alteration, a thorium concentration of 0.048 ppm in the limestone would result in the observed concentration of 32.1 ppm in KR-80, the bauxite. The thorium content of the limestone sample, KR-81, determined by gamma ray spectrometry is 0.19 ppm. This concentration is close to the limit of sensitivity of the spectrometer and is subject to large error. It is reasonable to conclude from the thorium measurements that the White limestone could well be the parent rock of the Jamaican bauxite.

The sample of basalt from Ireland is extremely low in thorium and uranium. The thorium and uranium contents of the bauxite derived from the basalt are also low compared to the average in Table III, but the Th/U ratio for the bauxite sample, KR-84, is 5.2. This is the same as the average Th/U ratio for bauxites derived from basic rocks.

Thorium and Uranium in Arkansas Bauxite.—Thorium and uranium data for the weathering sequence and drill core samples from Arkansas are presented in Tables V and VI, respectively. All of these samples, with the exception of KR-54, are taken from residual deposits of bauxite that overlie the parent syenite. KR-54, like KR-26 in Table II, is from a plastic or colluvial type of deposit which overlies the Midway clays. KR-54 is taken from the top of a transported bauxite deposit, just below the contact with sediments of the Wilcox Group.

The two transported bauxite samples, KR-26 and KR-54, have very similar thorium, uranium and Th/U values, but these values are not distinctively different from the analyses of the many residual bauxite samples. It is thought (Shepard, pers. comm.) that as a result of transportation of

Table VI. Thorium and Uranium in Drill Core Samples of Arkansas Bauxite

Sample	Footage	ppm Th	ppm U	Th/U	Lithology
KR-67	136-138	24.5	5.4	4.5	Dark brown, sandy carbonaceous clay
KR-68	138-140	71.8	6.6	10.9	Brown, carbonaceous clay, and gray, fragmental, pisolitic bauxite
KR-69	140-142	94.8	8.3	11.4	Pink and gray, fragmental, pisolitic bauxite
KR-70	142-144	87.5	8.4	10.4	Red and gray, fragmental, pisolitic bauxite
KR-71	144-146	85.3	8.6	9.9	Red and gray, pisolitic, fragmental, slightly sideritic bauxite
KR-72	146-148	91.8	8.6	10.7	Red with some pink, pisolitic, fragmental, slightly sideritic bauxite
KR-73	148-150	88.1	8.1	10.9	Red and gray, pisolitic, slightly sideritic bauxite
KR-74	150-152	94.7	7.8	12.2	Gray with some red, pisolitic, slightly sideritic bauxite
KR-75	152-154	90.4	7.1	12.7	Same as above
KR-76	154-156	87.3	6.9	12.6	Same as above
KR-77	156-158	73.6	8.8	8.3	Same as above, with occasional kaolinitic flecks
KR-78	158-160	51.6	7.2	7.1	Gray bauxite and sideritic clay with kaolin fragments
KR-79	160-163	24.7	4.8	5.2	Gray with some pink, kaolinitic, slightly sideritic, weathered syenite

Table VII. Thorium and Uranium in Material Balance Samples

Surinam	Weight lbs.	ppm Th	ppm U	Th/U	U_z	Th_c	alpha cpb	% Th	% U
bauxite	1.9	74.2	3.6	20.9	3.1		342		
calcined alumina	1.0	4.9	0.3	14.7			1.1	3.5	5
fine red mud	0.48	361	11.6	24.2		249	1332	96	82
classifier sand	0.05	122	10.1	11.9			609	4.3	7.1
								103.08	94.94
Arkansas									
bauxite	2.25	75.8	19.8	3.8	6.8		346		
calcined alumina	1.0						0.8		
fine red mud	1.04	120	39.6	2.8			750	73	93
classifier sand	0.22	70.1	6.4	11.0			318	2.1	3.1
							605		966

* For sample surface of 20.3 cm²

the bauxite these samples have a smaller accessory mineral content. This hypothesized decrease of accessory minerals does not noticeably affect the amounts of thorium and uranium found in the bauxite. The radioactive elements must, then, be transported either in extremely fine grained primary resistate minerals or in resistate hydrolyzate minerals.

The *Weathering Sequence* samples were collected in Tp. 2 S., R. 14 W., Sect. 16 and 26, of Saline County, Arkansas. Figure 4 is a diagrammatic section showing the relative locations of the samples taken from the Section 16 mine. From the analyses of these samples the following observations are made:

i) The thorium and uranium concentrations increase by a factor of 2 to 3, in the distance of a foot or so from the relatively fresh nepheline syenite to the weathered, kaolinitic syenite.
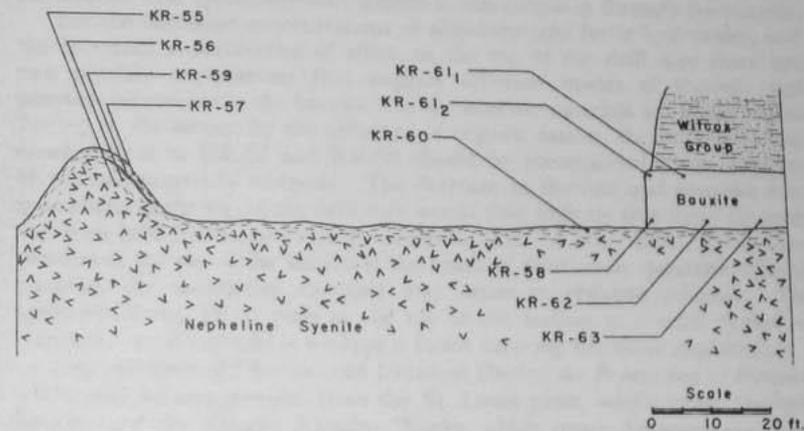

Figure 4.　Diagrammatic section showing relative locations of Arkansas samples.

ii) The thin limonite band in the kaolinitic rock and the clay material between the nepheline syenite and the overlying bauxite contain less thorium and uranium than the material immediately above or below. The hard limonite band, about ½ inch thick, is similar to that described by Goldman. If the uranium in bauxites occurred as ions adsorbed on the ferric hydroxide, the limonitic band that is represented by sample KR-59 might be expected to contain more than the measured 2.3 ppm uranium. The low radioactivity of the clay, sample KR-60, is in agreement with Frederickson's total activity measurements.

iii) The variations between samples KR-58, KR-62 and KR-63, and also between KR-61₁ and KR-61₂ illustrate large changes in thorium and uranium concentrations that occur in the distance of a few feet, with no apparent change in bauxite texture or vertical position in the deposit.

iv) Samples KR-64 and KR-66 from the Section 26 mine have higher

SCIENTIFIC COMMUNICATION

RADIOACTIVITY OF ALUMINUM METAL

J. A. S. ADAMS AND K. A. RICHARDSON

During a recent study of the thorium and uranium concentrations in bauxites (2, 5), it was found that in the processing of bauxite, much of the thorium and uranium is concentrated into the red mud, and calcined alumina contains very small amounts of these elements. For this reason, aluminum metal might also be expected to have rather low radioactivity. The radio-activities of a number of aluminum samples were measured by alpha counting, and the results are presented in this paper.

Table 1 gives the gamma ray spectrometer data on Surinam material balance samples. Adams, Richardson, and Templeton (2) give the pro-cedures. These samples, obtained through the courtesy of the Aluminum Company of America, consist of Surinam bauxite, calcined alumina, red mud, and classifier sand, from the East St. Louis alumina plant. Some of the gamma ray determinations were verified by chemical analyses, indicating that the thorium and uranium are in equilibrium with their daughter products in the bauxite and red mud samples. The results in Table 1 show that more than 80 percent of the thorium and uranium in the bauxite is concentrated in the red mud, and less than 5 percent of these elements is extracted with the alumina. The calcined alumina contains 4.9 ppm of thorium and 0.3 ppm of uranium, and has an alpha activity of 0.054 counts per hour per square centimeter. A sample of alumina produced from Arkansas bauxite has an alpha activity of 0.039 counts per hour per square centimeter. These alpha activities were measured a few weeks after the alumina was produced. Counting of the same samples approximately two years later indicated an increase in activity of approximately 100 percent, but this apparent change may have no statistical significance.

The alpha counting technique that was used in this study is the same as that described by Adams, Richardson and Templeton (2). The powdered material balance samples were counted in a 2 inch diameter planchet with a depth of $\frac{1}{8}$ inch. The alpha activities of the aluminum samples were measured on metal discs of the same diameter and thickness as the planchets.

The metal samples that were studied included 7 modern aluminum samples in varying degrees of purity, 3 samples of aluminum produced 30 to 40 years ago, and three National Bureau of Standards aluminum alloy samples. The alpha activities of the samples are listed in Table 2, with more detailed sample descriptions. The statistical error in these low level measurements ranges approximately from ± 20 to ± 90 percent of the measured activity.

TABLE 1

THORIUM AND URANIUM DATA ON SURINAM MATERIAL BALANCE

Sample	Weight, lbs	Th, ppm	U, ppm	Alpha* activity	% Th	% U
Bauxite	1.9	74.2	3.6	16.8		
Calcined alumina	1.0	4.9	0.3	0.054	3.5	5
Fine red mud	0.48	281	11.6	65.6	96	82
Classifier sand	0.05	122	10.1	31.0	4.3	7.4

* Alpha activities in counts per hour per square cm.

The average alpha activity of the seven relatively recently produced metal samples, KR-45 to KR-51, is 0.089 counts per hour per square centimeter. Measurement of the activities of these samples two years before the counts listed in Table 2 were made gave an average value twice as great. However, the activity of the metal being only slightly above background, its apparent decrease is within statistical limits of error.

The gradational decrease in purity in the series of samples KR-46 through KR-51 does not cause a change, within statistical limits of error, in the radio-activities of the samples. A sample taken from an anode of the electrolytic aluminum purification process has a measured alpha activity of 4.3 counts per hour per square centimeter. This is approximately the activity that would be expected for a sample containing 5 to 10 ppm of thorium and

TABLE 2

ALPHA ACTIVITY OF ALUMINUM METAL SAMPLES

Sample number	Alpha activity	Sample description
KR-39	0.13 0.16	N.B.S. #601: 4.38% Cu, 0.39% Mg, 0.88% Si, 0.52% Fe, 0.81% Mn, 0.020% Cr, 0.015% Ti.
KR-40	0.16 0.18	N.B.S. #602: 4.44% Cu, 1.49% Mg, 0.130% Si, 0.28% Fe, 0.63% Mn, 0.007% Cr, 0.012% Ti.
KR-41	0.34 0.33	N.B.S. #603: 0.29% Cu, 1.01% Mg, 0.52% Si, 0.21% Fe, 0.24% Cr. 0.037% Ti.
KR-42	0.79 0.69	Aluminum produced from Arkansas bauxite in 1918.
KR-43	0.41 0.24	Aluminum produced from Arkansas bauxite in 1920.
KR-44	0.24	Aluminum produced from French or Irish bauxite in 1907.
KR-45	0.074	Aluminum produced recently from Surinam bauxite.
KR-46	0.089	Aluminum samples KR-46 to KR-51 are produced from Arkansas
KR-47	0.14	bauxite. This series grades from 99.9% purity in KR-46 to 94% in
KR-48	0.069	KR-51. KR-48 has the composition typical of modern aluminum.
KR-49	0.11	
KR-50	0.059	
KR-51	0.089	

* Alpha activities in counts per hour per sq cm from solid metal surface.

uranium. Gamma ray spectral analysis of this sample indicates concentrations of less than 1 ppm for both of these elements. The radioactive decay series must, then, be out of equilibrium. Because the sample is over two years old, the alpha activity must be due to a concentration of some of the longer-lived nuclides.

The National Bureau of Standards samples, KR-39, KR-40, and KR-41, containing 93 to 98 percent aluminum (see chemical analyses in Table 2),

TABLE 3
ALPHA ACTIVITIES OF SOME METALS

Material	Alpha counts per hour per 100 cm²
Steel (commercial)	
Brass (commercial)	3
Copper (commercial)	5
	9
Aluminum (commercial)	
Tin (commercial)	31
	121

exhibit alpha activities somewhat greater than the samples of modern aluminum. Probably the increased radioactive content was added to these alloys with one or more of their minor metal constituents.

The three old aluminum samples, KR-42, KR-43, and KR-44, are two to eight times more active than the modern samples. This might be due to a greater radioactive impurity in the samples at the time of production, or to a build-up of radioactive daughters from a non-equilibrium condition.

TABLE 4
BETA ACTIVITIES OF SOME METALS

Material	Beta counts per minute per 100 cm²
Copper tubing	
Brass rod	0.05
Steel scale	2
	5
Aluminum (2S)	
Aluminum (superpure)	6
	4
Lead (modern)	
Lead (16th century)	11
	1

Bearden (3) measured the alpha activities of materials commonly used in the construction of radiometric equipment, and some of these are listed in Table 3. Table 4 gives more recent measurements (4) of the beta activities of some metals. These data show that, although aluminum is produced from an ore with relatively high radioactivity, the radioactivity of aluminum metal is comparable with that of other common metals.

ACKNOWLEDGMENT

THE RICE INSTITUTE,
HOUSTON, TEXAS,
April 23, 1960

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PERTURBATION OF NUCLEAR DECAY RATES 5525

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CONTENTS

1. INTRODUCTION

One of the paradigms of nuclear science since the very early days of its study has been the general understanding that the half-life, or decay constant, of a radioactive substance is independent of extranuclear considerations. Early

workers tried to change the decay constants of various members of the natural radioactive series by varying the temperature between 24°K and 1280°K, by applying pressure of up to 2000 atm, by taking sources down into mines and up to the Jungfraujoch, by applying magnetic fields of up to 83,000 Gauss, by whirling sources in centrifuges, and by many other ingenious techniques. Occasional positive results were usually understood, in time, as the result of changes in the counting geometry, or of the loss of volatile members of the natural decay chains. This work was reviewed by Meyer & Schweidler (1), Kohlrausch (2), and Bothe (3). Especially interesting for its precision is the experiment of Curie & Kamerlingh Onnes (4), who reported that lowering the temperature of a radium preparation to the boiling point of liquid hydrogen changed its activity, and thus its decay constant, by less than about 0.05%. Especially dramatic was an experiment of Rutherford & Petavel (5), who put a sample of radium emanation inside a steel-encased cordite bomb. Even though temperatures of 2500°C and pressures of 1000 atm were estimated to have occurred during the explosion, no discontinuity in the activity of the sample was observed.

While the constancy of nuclear decay rates was thus firmly established, the confirming evidence was from studies of alpha- and beta-emitting species. It was pointed out in 1947 by Segrè (6) and by Daudel (7) that in the case of electron-capture decays the decay rate is directly related to the density of atomic electrons at the nucleus, and that, at least for low-Z nuclei such as ^{7}Be, the effects of different chemical environments should be measurable. The possible effects and some preliminary experimental attempts were discussed by Bouchez et al (8–10). Firm results establishing the effect were obtained by Segrè, Wiegand, and Leininger (11, 12), and were confirmed and extended by Kraushaar, Wilson & Bainbridge (13), and by Bouchez et al (14). The confirmed effects were of the order of 0.1%.

Meanwhile the other radioactive decay process in which atomic electrons participate directly had also been studied. The 6-hr isomer ^{99m}Tc decays principally by internal conversion of a 2.2-keV $E3$ transition. Differences in the decay rate for sources in different chemical forms were established by Bainbridge, Goldhaber & Wilson (15, 16) and the chemical and solid-state implications of the results were discussed by Slater (17). The observed effects were of the order of 0.3%.

The revival of interest in this field in recent years may be exemplified by (a) the discovery of chemically induced half-life changes as large as 3.5% (18), (b) studies of changes in outer-electron internal conversion spectra (19), and (c) a growing awareness of relations between perturbations in nuclear decay rates and the phenomena studied with Mössbauer and ESCA (Electron Spectroscopy for Chemical Analysis) techniques. Parts of the current subject have been discussed, in wider contexts, in earlier reviews by DeBenedetti, Barros & Hoy (20), and by Hollander & Shirley (21). Brief, but more specific, reviews have been given by Daudel (22), Perlman (23), and Perlman & Emery (24).

2. DECAY MODES DIRECTLY INVOLVING BOUND ELECTRONS

2.1 ELECTRON CAPTURE

The weak interaction involved in electron capture and other forms of beta decay is of very short range. This means that the rate of electron capture is essentially proportional to the density at the nucleus of electrons available for capture. The most direct way to change the electron-capture rate is thus to change the total electron density at the nucleus. Extensive accounts of the electron-capture process and its relation to the other modes of beta decay may be found in the treatises of Konopinski (25), Schopper (26), and Wu & Moszkowski (27). Bouchez & Depommier (28) reviewed the subject of electron capture, and more recent results may be found in the *Proceedings* of the Debrecen meeting (29) and in a review by Berényi (30). We follow here the notation used in the tabulation of Behrens & Jänecke (31), which is based on the formulation developed by Bühring, Stech, and Schülke (32–35). [The recent revisions in this formulation (36) are not important for the present discussion.]

The total transition probability for electron capture of orbital electrons is given by

$$\lambda = (g^2/2\pi^2) \sum_x n_x C_x f_x \qquad\qquad 1.$$

where g is the weak interaction coupling constant, the running index x refers to the various bound atomic orbitals, n_x is the occupation probability of orbital x ($n_x = 1$ when the orbital is full), C_x, to be discussed more fully below, is the capture analog of a beta-spectrum shape factor, and f_x is equivalent to a beta-decay Fermi function. It is given by

$$f_x = (\pi/2) q_x^2 \beta_x^2 B_x \qquad\qquad 2.$$

The quantity q_x is the energy of the neutrino emitted when an electron hole is left in orbital x. β_x is the wavefunction amplitude for an electron in orbital x; for s-states ($\kappa = -1$), $\beta_{-1} = g_{-1}(0)$, and for $p_{1/2}$-states, ($\kappa = +1$), $\beta_{+1} = f_{+1}(0)$. B_x is the exchange and overlap factor of Bahcall (37–41), which takes into account the lack of one-to-one correspondence between processes in which an electron is captured from orbital x in the initial Z atom and those in which a vacancy is left in orbital x of the final $(Z-1)$ atom.

The Coulomb field near a nucleus is very strong. The shape of electron wavefunctions near the nucleus is thus independent of external perturbations; such perturbations only affect the normalization of the wavefunction in the nuclear region. The most direct effect of chemical or thermodynamic perturbations is then on the product $n_x \beta_x^2$, which measures the density of electrons in orbital x at the nucleus. The factors C_x, given explicitly by Behrens & Jänecke

(31), are combinations of nuclear matrix elements, weighted by factors depending on the shapes of the wavefunctions of electrons bound in the x-orbit. They may be expressed as squares of terms which are power series in αZ and in the nuclear radius, R. For allowed transitions, for example, the leading terms are just the Fermi and Gamow-Teller matrix elements. The correction terms, in all cases while depending on the charge and size of the nucleus, and weakly on its charge distribution (36), and on the momentum transfer, are independent of changes in the wavefunction normalizations in the inner region. The relative contributions of occupied orbits with different angular momentum quantum numbers do depend, in general, on the nuclear matrix elements. For almost all transitions however, the decay is dominated by capture from $s_{1/2}(\kappa = -1)$ and $p_{1/2}(\kappa = +1)$ orbits, and the rates are proportional to $n_{-1}\beta_{-1}^2$ and $n_{+1}\beta_{+1}^2$ respectively.

Exchange and overlap effects can be very important in electron capture. They were first considered by Benoist-Gueutal (42) and by Odiot & Daude (43). The application of closure methods by Bahcall (37–41) allowed definite predictions of the factors B_x in Equation 2. Since B_{1s} is always less than one while for the higher shells B_{ns}, $n \geq 2$, is greater than one, such ratios as capture leading to L holes relative to capture leading to K holes are altered. The dominant factor in these alterations is the exchange effect, in which, for example, an electron in the K-shell of the initial atom is captured, but the hole appears in the L_1 shell of the final atom. The effects decrease with increasing Z. The predictions of Bahcall for L/K ratios are confirmed, in general, by experiment (29, 30, 41, 44). The accuracy of experimental M/L capture ratios is not yet sufficient to allow a conclusive test of calculated correction factors (45).

In a rather large percentage of electron captures it may be expected that an electron bound in the initial atom may find itself promoted to the continuum after the capture. This is mostly a shakeoff process due to the sudden change in nuclear charge. In a paper reporting a measurement of the K-electron shakeoff probability in the K-capture of ^{131}Cs, Lark & Perlman reviewed previous experimental and theoretical work (46). Further calculations are reported by Carlson et al (47). The probability of shaking off a K-electron decreases as Z^{-2}, and the probability of shaking off outer electrons can be expected to be somewhat smaller for electron capture than for ordinary (positive or negative) beta-ray emission.

In spite of the dramatic effects on capture ratios in light elements (for example the L/K ratio in ^{37}Ar capture is increased by about 22% by exchange) the effect on total capture rates are much smaller. Bahcall has discussed the situation in some detail (38), and concludes that the fractional change in total capture rate due to exchange and overlap effects is of the order of the average atomic excitation energy divided by the neutrino energy. Aside from cases where the Q-value is not much larger than the K-shell binding energy, the effects are then always small, since the average atomic excitation energy can be estimated to be of the order of a few hundred electron volts (38, 47, 48). Bahcall's estimate of the total change in the decay rate of ^{7}Be due to overlap and exchange was less than 0.1%

The B-factors are essentially redistribution factors, whose weighted value is approximately one

$$\sum_x n_x \beta_x^2 B_x \approx \sum_x n_x \beta_x^2 \qquad\qquad 3.$$

The total capture rate is then approximately equal to the sum of Equation 1 with the B-factors left out; with the further approximation that the shape factor, C, has a constant value for capture from $s_{1/2}$ and $p_{1/2}$ orbitals, and is zero otherwise, the total capture rate becomes

$$\lambda = (g/\pi)^2 C \sum_x q_x^2 n_x \beta_x^2, \qquad x = s_{1/2}, p_{1/2} \qquad 4.$$

This equation is necessarily an approximation: the problem is really a many-body problem, and while the golden-rule matrix elements are dominantly proportional to the initial electron density at the nucleus, both exchange and the effect of atomic excitation on the density of final states do have an effect, even on the total decay rate. The situation is somewhat similar to that in electron shakeoff in beta-ray emission: the total shakeoff probability is given to a high degree of accuracy by calculations in the sudden approximation (47, 49, 50), but the shape of the spectrum is sensitive to the Pauli principle and the details of the two-electron final-state phase space (51, 52).

Until now, in published studies of chemical and other macroscopic perturbations of electron-capture decay rates, the effects of overlap, exchange, and shakeoff have not been considered. The size of these effects on total decay rates will, as we have seen, usually be small, of the order of a part per thousand. But since typical chemical effects are also of the order of a part per thousand, a more careful study of the validity of Equation 4 in the context of chemically induced changes in the quantities n_x and β_x would perhaps be worthwhile.

In situations where there is an appreciable density of free electrons, the rate of electron-capture decay may be affected, or even dominated, by the capture of these continuum electrons. Rates for capture of continuum electrons were first estimated by Bethe & Bacher (53). Detailed discussions, using the modern formulation of the weak interaction and including applications to stellar interiors, have been given by Bahcall (54) (see also Sec. 4.6).

2.2 INTERNAL CONVERSION

A nucleus in an excited state can decay to a lower level by photon emission, or, alternatively, by internal conversion. (Exotic decay modes, such as internal pair formation, two-photon emission, double internal conversion, etc., are not yet relevant in a discussion of rate perturbations, and will not be discussed here.) The total transition probability for decay is a sum of the transition probabilities for the various modes, thus, for the electromagnetic transition from level a to level b

$$\Lambda(a \rightarrow b) = \Lambda_\gamma(a \rightarrow b) + \Lambda_{IC}(a \rightarrow b) \qquad 5.$$

The internal conversion process can involve any of the atomic electrons, so

$$\Lambda_{IC}(a \rightarrow b) = \sum_{x'} \Lambda_{IC}(x', a \rightarrow b) \qquad 6.$$

where the occupied atomic orbits are described by x', which is an abbreviation for a principal quantum number n' and a relativistic angular quantum number κ'. The internal conversion coefficient for occupied orbital x' is defined as the ratio of the conversion rate to the gamma-ray rate:

$$\epsilon_{x'}(a \rightarrow b) = \Lambda_{IC}(x', a \rightarrow b)/\Lambda_\gamma(a \rightarrow b) \qquad 7.$$

The total conversion coefficient is just the sum over occupied orbits of the partial coefficients

$$\epsilon_{Tot}(a \rightarrow b) = \sum_{x'} \epsilon_{x'}(a \rightarrow b) \qquad 8.$$

and the total rate for the electromagnetic transition, $a \rightarrow b$, is

$$\Lambda_{Tot}(a \rightarrow b) = \Lambda_\gamma(a \rightarrow b)[1 + \epsilon_{Tot}(a \rightarrow b)] \qquad 9.$$

Internal conversion is to gamma-ray emission as hyperfine structure is to the observation of nuclear moments in an external field. Internal conversion is an off-diagonal form of hyperfine structure. Most internal conversion is "normal," that is, the internal conversion rates and the rate of gamma-ray emission are proportional to the square of the same nuclear matrix element. Just as in diagonal hyperfine structure (55), this is not necessarily the case when there are appreciable contributions from parts of the electron wavefunctions which lie inside the nuclear charge distribution. Such "penetration" effects have been reviewed by Church & Weneser (56), and their relevance to the present context is discussed briefly in Sec. 5. For cases of normal conversion the coefficients are independent of the details of the structure of the initial and final nuclear states, depending only on the energy and multipole nature of the nuclear transition, and on the atomic wavefunctions. The coefficient for conversion in the x' state of a transition between two nuclear states whose energy differs by k, of multipolarity σL, σ either M or E, is (57, 58)

$$\epsilon_{x'}(\sigma L, k) = \frac{\pi k(e^2/\hbar c)}{L(L + 1)(2L + 1)} \sum_\kappa B_{\kappa\kappa'}(\sigma L) \left| R_{\kappa,x'}(\sigma L, k) \right|^2 \qquad 10.$$

where κ describes the angular state of the continuum electron, the coefficients $B_{\kappa\kappa'}(\sigma L)$ are those given by Rose (57),[2] and the R's are radial integrals. If the binding energy of the x' orbit is $b_{x'}$ the radial integrals are

[2] An error in one value of B in this reference is corrected in Ref. 58, footnote 39.

$$R_{\kappa,x'}(ML, k) = \int_0^\infty r^2 dr [g_\kappa(k - b_{x'}, r)f_{x'}(r)$$

$$+ f_\kappa(k - b_{x'}, r)g_{x'}(r)]h_L^{(1)}(kr) \qquad\qquad 11.$$

$$R_{\kappa,x'}(EL, k) = \int_0^\infty r^2 dr \left\{ [g_\kappa(r)f_{x'}(r) - f_\kappa(r)g_{x'}(r)]k \right.$$

$$\left. - [f_\kappa(r)f_{x'}(r) + g_\kappa(r)g_{x'}(r)] \frac{d}{dr} \right\} rh_L^{(1)}(kr) \qquad 12.$$

where $h_L^{(1)}(kr)$ is a spherical Hankel function of the first kind, g_κ and f_κ are the Dirac radial wavefunctions for outgoing electrons of kinetic energy $k - b_x'$, and and $g_{x'}$, $f_{x'}$ are the Dirac radial wavefunctions for the initial occupied bound orbit. The B-coefficients tabulated are for fully occupied bound orbits, where the number of electrons is $2|\kappa'|$. If the bound orbit is not fully occupied, they should be multiplied by the occupation probability. The continuum wavefunctions are normalized per unit energy interval, and those Dirac radial components which are large near the nucleus, $g_{-|\kappa'|}$ and $f_{+|\kappa'|}$, are positive there (58).

The theory of internal conversion has been reviewed by Rose (59) and by Listengarten (60), as well as in references previously cited. Detailed accounts of many parts of the subject appear in the proceedings of the Vanderbilt Conference (61). The initial full-scale tabulations of theoretical coefficients for conversion in the K and L shells were given by Rose (57) and by Sliv & Band (62). More recent, and somewhat technically improved, calculations for the K, L, and M shells have been performed by Hager & Seltzer (63), and by Pauli (64). Results for the N shell, for $Z \geq 60$, have been given by Dragoun, Pauli, & Schmutzler (65). Calculations for several specific nuclear transitions have been performed by Bhalla (66–70). In addition, a computer program for calculating theoretical conversion coefficients has been presented by Pauli (71). All these calculations include the static effects of the finite nuclear size (72, 73). In the tabulations of Rose (57), Sliv & Band (62), and Pauli (64), screening has been treated by the Thomas-Fermi-Dirac method, while Hager & Seltzer (63) and Bhalla used relativistic self-consistent field wavefunctions for the electrons. For the wavefunctions used by Dragoun et al, screening potentials were derived from nonrelativistic SCF calculations. The program of Pauli is adaptable to a variety of treatments of screening.

The most complete calculations for the inner shells are those of Hager & Seltzer (63). As far as one can tell from internal consistency and smoothness, when compared with the other modern results and with the most precise experimental data, these coefficients are accurate to within a few percent. [The set of values given for $Z = 93$, L_2 shell in (63) is in error, however; the preliminary report (74) may be consulted for these coefficients.] The only well-established discrepancy is that L_1 conversion, relative to L_2 and L_3, of some $E2$ transitions of

The Society of the Living Dead—Ottawa, Illinois *by Catherine Quigg, 2000*

For more than two generations, hundreds of young women came from surrounding farms and nearby small towns to work with radioactive materials in downtown Ottawa, Illinois, about eighty miles south-west of Chicago. They painted luminous watch and clock dials and hands at the Radium Dial and Luminous Processes factories from 1920 to 1978. Exposed to radioactive radium and tritium, many of these workers developed cancers, tumors, and other radiation-related illnesses. Some died premature and painful deaths. As an anti-nuclear activist, researcher, and writer in the 1970s, I began hearing stories about these unfortunate women and their tragic lives. I investigated their claims in the early 1980s with a small grant from the Center for Investigative Journalism.

During the early spring of 1984, I spent two weeks in the rural town of Ottawa, near the junction of the Illinois and Fox rivers, interviewing as many survivors as I could find. I met with these women in their homes, on the phone, or over coffee in the comfortable living room of a longtime resident. Most seemed anxious to tell of their experiences; a few were shy and fearful of the stigma of having cancer. Next I reviewed pertinent records and documents at the regional office of the U.S. Nuclear Regulatory Commission (NRC) in Glen Ellyn, Illinois, and the Illinois Department of Nuclear Safety (IDNS) in Springfield. The state of Illinois authorized the use of radium in Ottawa in 1957, and the NRC licensed the use of tritium there from 1961 to 1978. I also talked with scientists from Argonne National Laboratory near Darien, Illinois, who measured the radioactivity in the workers' bodies, and I spoke with appropriate federal government officials. In the process, I discovered how state, federal, and corporate negligence allowed radiation contamination and overexposure to affect the health of workers.

Even today, despite recent revelations about radiation victims by the U.S. Department of Energy, this large group of victims and families has gone unnoticed and uncompensated for their work-related illnesses or untimely deaths. Emphasis on businesses' profits in the 1980s fostered public apathy toward environmental and health investigations, making it difficult to publish articles raising questions of corporate negligence or malfeasance in these areas. My numerous queries to the media pro posing an article about these women were rejected. Discouraged, I set my notes aside and moved on to other concerns. Now I look back in sadness at Ottawa radiation victims never recognized for the injustice nor compensated for the pain they suffered. I wish I had been more persistent in bringing their plight to public attention. Most of them are dead today. Their story should concern us all. With assistance from early notes, I would like to share the highlights of their painful ordeal.

Radium Dial Company, a subsidiary of U.S. Standard Chemical Company of New York, employed the first wave of dial painters from 1920 until December 1936 at Ottawa; there were smaller plants in Chicago, Streator, and Peru, Illinois. Supervisors at the early Radium Dial plant allowed workers to place camel's hair brushes between their lips to get a fine point for painting luminous numbers on timepieces. With each lick of her brush, a dial painter swallowed a little radium and added forever to the deadly burden carried in her bones. Within a few years, some workers became seriously ill.

"They said it was all right, nothing wrong, to put the brush in your mouth and paint numbers and then dip the brush in again," recalled Charlotte Purcell, who started at Radium Dial in 1922, at age sixteen. She stopped working in 1932, when her arm was amputated to halt the spread of cancer. When I met her at her home in Chicago, Purcell walked slowly, with a cane.

I spoke on the phone with Marie Rossiter Hunter, a dial painter from 1923 to 1930. She said, "We used to paint our eyebrows, our lips, and our eyelashes, and then look at ourselves in the darkroom just for fun." Rossiter remembered eating her lunch at her desk. "They never said anything, they never stopped you," she said, sounding angry at the recollection. At the time of our conversation, she had had six leg operations, and her bloated legs were turning black. She said doctors told her that her bones were honeycombed with radium.

Besides radium ingestion, workers were exposed to radioactive dust and to penetrating external gamma radiation from workplace surfaces contaminated by the decay products of radium.

For many women, the first symptoms of radium poisoning were tumors and pain in their feet, probably caused by years of standing on radium-contaminated floors. Bone cancers often came with slow healing spontaneous fractures; leg and arm bones weakened, and snapped. Some workers became anemic when radium continuously bombarded their bone marrow, where blood cells are produced. Many had breast tumors, leading to mastec-

tomies. Others had serious problems with their teeth. Because of their myriad deadly diseases, local newspapers referred to the early Ottawa dial painters as "The Society of the Living Dead."

In 1935 Catherine Wolf Donahue petitioned the Illinois Industrial Commission for workers' compensation for permanent disability, medical care, and hospital care. A dial painter at Radium Dial from 1922 to 1931, she suffered from radium poisoning with disintegration of the jaw and malignancy of her hips. At the time of the trial, she weighed only seventy-one pounds, half her normal weight, and had to be carried into the courtroom. Donahue's attorney contended that Radium Dial's New York-based executives should have known the hazards of brush licking and stopped this practice, especially after the highly publicized 1927 New Jersey dial painters' lawsuit against U.S. Radium Corporation. In the fiercely contested court battle, Radium Dial argued that radium was an abrasive, not a poison. The court ruled in favor of Donahue, awarding her $5,561. Donahue died three months later, leaving her young husband and two small children.

To avoid further claims, Radium Dial shut its doors in December 1936. By that time, at least twenty-four of its workers had died horrible, lingering deaths from radium poisoning.

The second wave of Illinois dial painters were employed by Radium Dial's successor company in Ottawa, Luminous Processes, Inc., from 1938 until 1978. The new company, a closed corporation, had the same president as Radium Dial—Joseph Kelly, Sr.—the same equipment, and many of the same workers as the old company. It was located in a two story brick building just two blocks from the old site. The women I interviewed were mainly "second wave" workers who had worked at the "new" Luminous Processes, although some had worked solely at Radium Dial and others at both factories.

Former Radium Dial workers took jobs at Luminous thinking the new operation safe. Their supervisors informed them that earlier dial painters had died because they put brushes in their mouths, and since brush licking was no longer permitted, exposure to radium would not be harmful The supervisors didn't know, or neglected to mention, that the decay products of radium emit powerful gamma external radiation that, like X-rays, can penetrate the body without being ingested. That's why exposure to radium, primarily from some of the daughter products along the decay chain, can cause a wide range of diseases, including cancer of the breast, bone, bone marrow, and skin.

At first, workers called "screeners" used wood spatulas to spread radium paint on screens placed over watch dials. The excess paint was removed with hand-held sponges. They painted clock hands with fine tipped brushes dipped in open jars of radium paint. Smocks were their only protective clothing. Beginning in 1948, workers applied radium paint with hand-held sponges as watch and clock dials revolved on a table in front of them. Clock hands continued to be painted manually. On average, workers processed three million dials each year.

There was no state registration for the use of radium in Illinois until 1957, when the Radiation Installation Act was passed. And it took the State Radiation Protection Act of 1974 to give Illinois power to license companies and to set upper limits on worker radiation exposure. The lack of either state or federal oversight was especially reprehensible during the 1940s, when the war effort swamped Luminous with orders from the federal government for military items such as aircraft instrumentation, compasses, and other equipment. The U.S. armed forces became a regular Luminous customer through its contractor, the Bendix Corporation of Southfield, Michigan. State inspection reports from July and September 1965 tell of work areas contaminated with radium and its daughter decay products. Inspectors stated that safety precautions were ineffective; ultraviolet light did not identify radium contamination on workers' hands as intended; and "waterless" hand cleaners were not effective in removing radioactivity from employees' hands or from under their fingernails.

"You couldn't work in that plant without getting covered with the stuff," said Pearl Schott, a dial painter from 1946 to 1977. "Only paint thinner would remove the luminous paint from our bodies." She complained that "Company officials took our film badges [to record external radiation exposure] in a dark room and dusted them off before they sent them out for readings."

In May 1973 a state inspector found gross radioactive contamination in work areas, offices, the lunchroom, and the rest room. There was radioactivity on at least six employees' hands, and radioactive waste in unmarked containers. Despite these negative findings, Illinois continued to authorize radium use at Luminous, and permitted the gradual introduction of radioactive tritium beginning in 1957. During the late 1960s and early

1970s, most dial painters alternated between radium and tritium work. "If we changed material, it was like going from Lux to Camay," said one former worker. "No one spoke of the dangers of either."

By 1975, the company had switched from state-licensed radium to exclusive use of the now federally licensed tritium. Federal documents show tritium use skyrocketed; hundreds of thousands of timepieces containing thousands of curies of tritium were produced and shipped each month from Luminous to the Westclox factory in Peru, Illinois, for further assembly. The process for tritium work at Luminous was much like that for radium work. Workers spread luminous tritium paint with hand-held sponges over clock dials placed under screens, and removed the excess. These screeners had exhaust fans to vent gaseous tritium, but other painters, who applied tritium manually to watch dials with artist brushes or glass rods, had no exhaust fans.

Company officials told the women that tritium was harmless. But tritium gives off mainly internal radiation. Tritiated water vapor can be absorbed through the lungs or diffused through the skin. Scientists say tritium, which replaces ordinary hydrogen, incorporates into all body tissues, including ovaries and testes, which contain the genetic DNA. Bone marrow is one of its most important targets.

In my long conversation with Debra Mooney Smith, a radium and tritium screener from 1973 to 1975, she blamed her many health problems on her work at Luminous Processes. She said, "They told me there was really nothing that was going to hurt us with tritium—that you had to have a high amount of it before it could do anything to you." According to Smith, "There was no ventilation, no windows you could open, no air conditioning—only a few fans. A lot of times I was working right over the screen; my face was just inches away." She said many workers griped about the terrible smell of tritium paint and its fumes, "which rose right up to our faces, causing constant headaches."

Another screener, Mary Kapsul Hougas, confirmed Smith's observations: "We'd work right over the screen with our noses practically in it. There was nothing between us, the material on our hands, and our breathing." When told to go upstairs to work with tritium, her sister-in law, Lee Chiovatero Hougas, objected because "I didn't want any more tumors." Nonetheless, the manager told her tritium was harmless, and assigned her to wash tritium screens in a small, isolated room that had no fans.

After complaints about the smell of tritium and an outbreak of skin rashes, Luminous's vice president, Warren N. Holm, flew in from New York to reassure workers. He told them: "If you could measure worm particles in tomato juice, like you measure radiation in the air, you would never want to drink tomato juice again."

Tritium handlers were required to take monthly urine tests, the results of which were sent to the NRC. Test results indicated a range up to almost double the amount allowed by federal regulations. From 1975 to 1977, at least twenty-nine women had tritium readings over the federal limit. In April 1976, an NRC inspection showed widespread tritium surface contamination, worker overexposure, and excessive radioactive re leases to the outside environment. Things only got worse. Radium contamination continued to be a problem, even after Luminous's license to use it had expired. As late as 1977, state inspectors found radium contaminated desktops, unsecured jars of radium paint, and radioactive waste emptied down toilets, into the local sewage system. In January 1978, federal inspectors again confirmed excessive tritium levels in the plant's atmosphere—up to 170 times the NRC's permissible limit. Four months later, the situation had not improved.

Finally, because of its repeated disregard for regulations, the NRC ordered immediate suspension of the company's license on February 17, 1978. Lurninous immediately shut down its Ottawa plant. At that time, the company had thirty-five employees working with tritium in time piece production, as well as others in shipping and receiving.

By 1980, seven former Lurninous workers had jointly filed for workers' compensation with the Illinois Industrial Commission, claiming that their cancers, blood disorders, tumors, and other ailments were caused by occupational radiation exposure. The women said safety pre cautions at the plant were almost nonexistent, and they were constantly being contaminated by radioactive materials they used and by debris thrown in open bins. Company officials continued to assure them radium and tritium were safe to handle, they reported.

The women asserted in their lawsuit that their survey of one hundred former Luminous painters showed that at least sixty-five had died since the 1960s; of this group, twenty-eight died of cancer, well over twice the expected cancer rate. Their fatal illnesses included radium poisoning and cancers of the lungs, breasts, lymph glands,

bowels, throat, and brain. As years went on, more former workers were added to the list of those with cancers, tumors, and other radiation-related ailments.

Since 1980, nothing has been done to compensate Luminous workers for their pain and distress. Their workers' compensation legal case has fallen through bureaucratic cracks. The state, the federal government, and the corporations involved with "The Society of the Living Dead" have all washed their hands of any responsibility to these women. I remember having coffee one morning in a ranch-style house on a hill overlooking the village of Ottawa with Lee and Mary Hougas. They showed me their voluminous scrapbook with death notices and photos of their fellow radium dial painters. As they turned each page, I could tell they knew each woman intimately—her kind of work, her family, her illnesses, her hospitalizations, and the unusually early date of her death. Their litany began: "Died of breast cancer, died of cancer, leg amputated, died of bone cancer, brain cancer, died of . . . ," sand it went on and on as they pointed out one woman after another. In a group photo of former workers, their fingers lingered on a slim, sweet-faced young woman. I was told, "She had a horrible death. There was nothing left of her; her bones disintegrated. She was such a doll. Such a shame." I finished my coffee, thankful it was strong.

Reflecting on her own work at Luminous, Mary Hougas said "We were very naive. We were innocent victims of the times, victims of ignorance, and victims of our state officials and inspectors. The only reason I speak out now is for my two grandchildren. I think we're going into an era when a lot of radioactive materials are going to be used. It may happen again, and if I can prevent it by talking about it, I will."

We should listen.