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ADP013385

TITLE: Contamination of Environment as Possible CB Terrorism

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TITLE: Chemical and Biological Medical Treatment Symposium - Industry
II World Congress on Chemical and Biological Terrorism

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ADP013371 thru ADP013468

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15. CONTAMINATION OF ENVIRONMENT AS POSSIBLE CB TERRORISM

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INTRODUCTION

Diseases of unknown origin affected the Canadian soldiers, present as a part of the UNPROFOR in Croatia during 1993-1995. The government of Canada expressed its concern and suspicions that xenobiotics in the environment or other still undetermined environmental conditions were the cause of the ailments that threatened the health of its forces. As the host country, the Republic of Croatia took responsibility to investigate possible indigenous sources of diseases. The first step was measuring of radioactivity and sampling of soil and material used to fill sacks and shelters at the places of soldier's stations. The sacks and shelters were filled with bauxitic material, red mud (waste material from the abandoned alumina plant), terra rossa red soil, brown soil and limestone debris. Sampling, measurements and chemical analyses were done independently by Canadian and Croatia expert teams. No chemical warfare agents, PCBs, or other manmade toxic materials and no radioactivity above background levels were detected by these detailed chemical analyses. The expert teams, in turn, confirmed that the soldier's stations, as the places of everyday living activities and task performance, were inside bauxitic open pit mines, but unluckily placed downwind the open space disposal pools filled with caustic solution, waste of alumina production.

The Croatian side paid attention to analysis of the bauxitic material, red mud, limestone from the footwall rocks and caustic solution. The bauxites, used as filler of sacks and shelters, contain increased concentration of a series of elements, such as As, Pb, Cd, Cr, V, Hg, etc., but in highly immobile forms. Mobility of these elements in the red mud is negligible, but could be affected eventually by extremely low pH, not possible in the carbonate rich environment. In addition, in caustic solutions some toxic elements are enriched. It should be mentioned that no deleterious effects of raw material, products of wastes in alumina production have been recorded elsewhere.

The absence of deleterious matter raised the questions: "Could the chemical composition of bauxite ores be a cause of disease?" and "could natural environments become a medium for chemical and biological terrorism?" or "can the fear of the unknown in an environment be used as terrorism?" Once a cause and effect are linked, it is easier to deal with any harmful material.

Case history

The August 1995, according to confidential Canadian military reports, the Canadian peacekeepers serving in Croatia in the mid-1990s were repeatedly exposed to hazardous substances such as PCBs, uranium or bauxite. It was learned that Krajina Serb authorities had laid claim against the UN for the "stealing" of the bauxite, the material that was used to fill sandbags by the Canadian troops. The Canadian public awareness on growing number of ill veterans forced military officials to send a team of experts to Croatia to investigate the allegations of contamination. The need to characterize the hazard was emphasized in 1999 when allegations were made that unexplainable illnesses, being reported by Canadian Forces Personnel, deployed with UPROFOR, Croatia (1993-1995), were a result of being unknowingly exposed to toxic industrial chemicals. A review of scientific data could not

discount these accusations. The team was dispatched to Croatia during summer 1999 to conduct forensic environmental investigation of the Canadian occupation sites. A significant amount of time had lapsed since the last occupation and analytical program was restricted to contaminants that are persistent in the natural environment. A team of Croatian Ministry of Defence joined the Canadian team of experts in order to coordinate fieldwork on the ground with 1.5 million of landmines. Joined campaign of sample collection at the same sites was intended to avoid misinterpretation of the survey result.

The Canadian occupation sites were inside the open pit bauxitic mines, close to an abandoned alumina plant on the location of Zaton (near Obrovac). The plant was built in 1978 with the estimated production of some 300,000 tons of alumina per year. The ore potential was insufficient to satisfy capacity of the plant and production was not profitable. "The political plant" was shut down, but piles of ore were spread around negligently, and waste products, red mud and caustic solution, stored in two large basins. The Larger basin has a volume of $1.58 \times 10^6 \text{ m}^3$, 2/3 being filled with red mud, covered by caustic solution, while the remaining area of the basin is covered with dried red mud. The smaller basin has a volume of $0.75 \times 10^6 \text{ m}^3$ and is filled almost exclusively with the caustic solution. The estimated total amount of red mud is $0.85 \times 10^6 \text{ m}^3$, while the amount of caustic solution is estimated to be $0.5 \times 10^6 \text{ m}^3$ in the smaller basin and $0.3 \times 10^6 \text{ m}^3$ in the larger one. The position of occupation sites was unluckily placed downwind from the abandoned alumina plant and two large basins filled with caustic solution. An adverse effect developed by strong, cold, dry wind, named "bura", blowing great deal of a year from the continent, with a speed usually exceeding 100 km/h, produces efficiently water spray from the upper surface of the caustic solution basins. It evaporates immediately leaving high concentration of toxic particulates, as aerosol in the environmental air.

The target of the research was bauxites, red mud, limeatones and caustic solution as possible toxic material, a cause of the health problems.

Red mud

Detailed sampling plan was prepared with the aim to investigate the possible variations of the chemical properties of red mud. 43 samples of red mud were collected and analysed for 16 elements: Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr and Pb. The analytical method was tube excited XRF. In addition, major chemical compounds present in the red mud were determined by XRD method. Also, a weight loss on 105 °C and loss on ignition on 900 °C and pH value were determined in each collected sample. Percentages of exchangeable fraction were determined on two pH values and three different temperatures. Elemental concentration in resulting solutions was measured by both AAS and XRF.

The results of XRD analysis show that the main components in mineral composition of the red mud are hematite and calcite, while rutile, goethite and bayerite have less important role. Relatively high amount of gibbsite was also found what points out to incomplete extraction of Al^{3+} during Bayer's process.

Measured concentrations of elements are shown in Table 1. The investigated material was chemically homogenous within the particular basin. Significant differences in elemental concentrations are found between samples from the large and the small basins. The pH values in samples from the dried part of the basin are between 8.2-8.5, while in samples covered with the basic solution are between 9-10. Mean value of Na_2CO_3 is 4.33% and the highest values were found in samples from the small basin (9.35 %).

Table 1: Mean value and range of elemental concentrations in red mud samples

Element	Range	Mean value
Ti (%)	1.6-3.8	2.4
V (ppm)	215.3-667.2	499.4
Cr (ppm)	243.2-406.1	325.5
Mn (ppm)	4240.4-7668.3	6240.5
Fe (%)	15.0-22.6	18.8
Ni (ppm)	12.7-115.0	59.0
Cu (ppm)	18.1-47.8	38.4
Zn (ppm)	65.0-176.1	135.5
Ga (ppm)	12.0-185.2	48.4
As (ppm)	43.7-666.4	246.6
Rb (ppm)	2.8-7.8	4.4
Sr (ppm)	65.0-115.2	91.4
Y (ppm)	116.6-249.8	184.6
Zr (ppm)	666.0-1769.8	991.9
Pb (ppm)	20.9-545.2	64.0

Caustic solution

From the results of chemical and statistical analyses (Table 2), on the basis of 41 samples of caustic solution taken at different depth (every 1 m) from the large and the small basin, it can be concluded that the caustic solution is homogenous in each particular basin, within the whole its volume, in chemical composition, pH (10.2) and alkalinity. Alkalinity results from CO_3^{2-} and HCO_3^- salts, a product of reaction of NaOH, liberated from red mud and CO_2 from air. Comparing the mean values of elemental concentration from the large and the small basins statistically significant difference can be found only for chemical elements: Cu, Ga, As, Se, Br and Pb. Elements Ga, As and Pb have higher concentrations in the samples from the small basin while concentrations of Se, Br and Cu are higher in the solutions from the larger basin. Concentration of V, Cr, Cu, As, and pH value are much higher than allowed for technical waste waters discharged directly into the environment.

Bauxites

The bauxite region of Dalmatia is situated in the middle of the Eastern coastal part of the Adriatic Sea. There are several marked mountains, Velebit, Dinara, Svilaja, Mosor and Promina, in a distinctive karst region, built up of carbonate rocks dominantly, in contrast to the karst fields (polje) of Sinj, Drniš and Knin. The flat terrains in the hinterland of Zadar (Ravni Kotari) and Šibenik, and the hilly Bukovica and Zagora area accomplish regional geomorphology. A few rivers run through almost dry, waterless, karstic countryside cutting their beds into canyons of particular beauty (Zrmanja, Krka, Cetina). The Dalmatian bauxite deposits were formed in several bauxitogenic phases in the Mesozoic and Cenozoic times. The oldest ones are of Triassic age and the youngest are formed in the Neogene, i.e. Miocene time (Šinkovec, et al., 1976; Šinkovec et al. 1989; Šinkovec & Sakač, 1991; Šebešić et al., 1985)

There are two kinds of Paleogene bauxites, Early and Late Paleogene ones. The Early and Late Paleogene bauxites are placed in the inner part of Dalmatia, at Bukovica and Zagora, in a region about 150 km long and 20 km wide (Šinkovec & Sakač, 1982). The bauxite deposits are concentrated around Obrovac, at Dračevac-Jasenica, Kruševo and

Bilišane villages, at the place where Canadian troops made their military camp. The deposits extend to Ervenik and Drniš towns, with well-known deposits on the Promina Mt. and in vicinity of the Moseć Mt. Bauxites of the same age can be found toward Sinj and Imotski towns, and further south-eastwardly in Herzegovina.

Table 2: Mean value and concentration range of elements and pH value in caustic solutions from the two basins and allowed concentration in technological waste waters

Element	Range, large basin	Mean value large basin	Range, small basin	Mean value small basin	Allowed concentration
Ti (ppb)	0-1265	890.4	713-1211	898.4	-
V (ppb)	0-1301	875.4	0-1348	977.1	50
Cr (ppb)	0-1314	406.5	0-1285	451.3	1000
Mn (ppb)	179-1325	897	729-1097	889.3	2000
Fe (ppb)	49-900	472.3	30-1600	477.6	2000
Ni (ppb)	0-545	362	0-588	365.7	1000
Cu (ppb)	331-517	434.5	298-522	397.2	100
Zn (ppb)	302-502	380.2	239-541	373.4	1000
As (ppb)	1800-5900	2578.7	4400-6400	5585.7	200
Co (ppb)	0-1342	296.1	0-1505	555.1	500
Ga (ppb)	300-4560	729.8	1100-3300	1387.6	-
Ge (ppb)	0-80	16.5	0-80	7.6	-
Se (ppb)	4-200	63.1	0-90	29.7	20
Br (ppb)	1600-3000	2233	300-2800	1661.9	-
Rb (ppb)	500-5700	4781.9	1500-5900	4876.2	-
Pb (ppb)	0-59	10.5	10-338	65.6	200
pH	-	10.2	-	10.2	6.5-8

The Early Paleogene bauxite deposits are small, interpreted as fillings in the paleosinkholes. The footwall rocks are Late Cretaceous limestones, mostly Senonian rudisted limestones. The hangingwalls are mainly freshwater-brackish, thin-layered Liburnian limestones, more rarely Eocene formaminiferal limestones.

Their mineral content, as determined by DTA and microscopic examination on the chosen samples is in decreasing order: boehmite, gibbsite, hematite, kaolinite, pyrite, marcasite, goethite, anatase, rutile, calcite, and accessory minerals: zircon, disthene, staurolite, garnet, tourmaline, sphene, corundum, hydromica, chlorite and amphibole. The average chemical composition based on 6 samples is: SiO₂ 4.42 %, Al₂O₃ 56.27 %, TiO₂ 2.56 %, Fe₂O₃ 19.42 %, L.O.I. 15.00 %. Average content of trace elements in the Early Paleogene bauxite (in ppm) is: Cu 54 (25-80), Ni 265 (140-500), Co 27 (14-36), Cr 1200 (640-2300), V 959 (550-1400), Zr 476 (310-790).

The average chemical content of accessory oxides and trace elements of the Cretaceous limestones, the footwall rocks of the bauxites, based on 4 samples is: Al₂O₃ 286 ppm, Fe₂O₃ 110 ppm, TiO₂ 18 ppm, SiO₂ 581 ppm, Cu 0.6 ppm, Ni 0.4 ppm, Co 0.03 ppm, Cr 0.6 ppm, V 2.1 ppm, Zr 0.7 ppm.

The Late Paleogene bauxite deposits differ in size and shape. Their form is usually like lenses or big nests, occurring mostly in groups. The lens-shaped deposits are irregular and several hundreds meter long and wide, and thick more than 10 m. One of the largest was

in the Jasenica village, where the Canadian troops organized the camp in the open pit mine.

Their mineral composition is following: gibbsite, boehmite, hematite, goethite, kaolinite, anatase, rutile, pyrite, hydromica, lepidocrocite, psilomelane and calcite.

The average chemical composition of the Late Paleogene bauxites based on 7 samples is: SiO₂ 6.65 %, Al₂O₃ 47.86 %, TiO₂ 2.50 %, Fe₂O₃ 20.50 %, L.O.I. 22.50 %. Trace element content in ppm is: Cu 82, Ni 427, Co 35, Cr 1177, V 1072, Zr 462,

CONCLUSION

Bauxite ore is a natural product of weathering of aluminosilicate rocks and carbonates. It is formed by natural colloidal precipitation of Fe and Al hydroxides under neutral or slightly alkaline conditions during early diagenesis, which facilitates efficient coprecipitation of trace elements, especially those with high valency state, like U, Zr, Ti, REE, Th, etc., and a number of highly toxic elements like As, Cd, Pb and Se. They are, however, firmly tight within bauxitic minerals, gibbsite, boehmite, hydrargilite, hematite and clayey minerals, under wide span of natural conditions, including highly alkaline or acidic. They are also insensitive on different redox-conditions. We may assume as granted, there is no natural conditions available in supergene (hypergene) environment in carbonate rocks, which can release deleterious elements from bauxites into mobile form to affect human health.

Red mud is an anthropogenic product, the waste after aluminium oxide production, bauxitic like material. It stores high concentration of toxic elements, firmly tight within freshly precipitated colloidal oxyhydroxides. The problem arises from the evaporitic crusts on the red mud particles, formed after evaporation of the caustic solution, which itself is enriched in toxic elements. It consists of sodium salts and hydroxides easily soluble, releasing toxic substances when inhaled. In this way the dust of red mud could be a bearer of mobile forms of toxic elements.

The alkaline, caustic solution, a byproduct of the alumina production in the waste disposal pools, highly enriched in toxic elements, easily remobilized by aerosols during windy days, especially the days of "bura", north-easterly wind from the continent, might be a potential hazard to human health. There is a plausible conclusion that filling the sacks and shelters with bauxitic material, or camping in the bauxite open pit mine itself is not a cause of the troubles. Living prolonged time in the vicinity of the liquid waste disposal pools and inhaling aerosols developed by strong blowing of bura-wind as well as inhaling dust of red mud might be a source of health hazard.

KEY WORDS

Terrorism, chemical, biological, environmental contamination

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