Global Journal on Advances in Pure & Applied Sciences

Issue 1 (2013) 1051-1057

Selected Paper of 1st Global Conference on Environmental Studies (CENVISU-2013), 24-27 April 2013, Zeynep Sentito Hotel, Belek, Antalya, Turkey

Red mud waste storage problems, solution and utilization alternatives

Tatiana Yuzhakova *, Institute of Environmental Engineering, University of Pannonia, Veszprém, Hungary.
Ákos Rédey, Institute of Environmental Engineering, University of Pannonia, Veszprém, Hungary.
Zsófia Kovács, Institute of Environmental Engineering, University of Pannonia, Veszprém, Hungary.
Anett Utasi, Institute of Environmental Engineering, University of Pannonia, Veszprém, Hungary.
Istvan Ráduly, Babes-Bolyai University of Science, Cluj-Napoca, Sfantu Gheorghe, Romania.
László Dióssy, Institute of Environmental Engineering, University of Pannonia, Veszprém, Hungary.
Lenke Ráduly, Babes-Bolyai University of Science, Cluj-Napoca, Sfantu Gheorghe, Romania.
József Fazakas, Babes-Bolyai University of Science, Cluj-Napoca, Sfantu Gheorghe, Romania.

Suggested Citation:
Yuzhakova, T., Rédey, A., Kovác, Z., Utasi, A., Ráduly, I., Dióssy, L., Ráduly, L. & Fazakas, J. Red mud waste storage problems, solution and utilization alternatives, *Global Journal on Advances in Pure & Applied Sciences* [Online]. 2013, 01, pp 1051-1057. Available from: http://www.world-education-center.org/index.php/paas

Received November 22, 2012; revised January 10, 2013; accepted March 02, 2013.
Selection and peer review under responsibility of Dr. Nehir Varol.

Abstract

In October 2010 an extremely serious environmental catastrophe occurred in Hungary since about one million cubic meter of red mud sludge burst out from the reservoir killing people and contaminating the surface waters and soil. After the catastrophe special attention is paid for the red mud disposal sites for preventing similar disaster. The safe disposal of the red mud is a must, however, since the red mud contains several valuable materials such as ferric, aluminum, titanium, silicon, calcium oxides and other metals e.g. germanium, gallium, etc. the recovery of the valuable components and the processing and utilization of the red mud considered as a secondary raw material is a top issue. In this way the high environmental risk related to the storage can be mitigated. There are basically two main types of the processing and utilization of the red mud. The first one is its use as a uniform material for example for construction material manufacturing. The second possibility includes

* ADDRESS FOR CORRESPONDENCE: **Tatiana Yuzhakova**, Institute of Environmental Engineering, University of Pannonia, 10 Egyetem St, Veszprém and 8200, Hungary. *E-mail address*: yuzhakova@almos.uni-pannon.hu / Tel.: +36-88-624-296

the separation of different components and transformation each of them into valuable products. The paper deals with storage facility problems and possible solutions of disposal and utilization of the red mud.

Keywords: Red mud, storage possibilities, utilization, construction materials, recovery of metals.

1. Introduction

Red mud is a residue of the aluminium industry produced during the alkaline extraction of alumina from bauxite by the Bayer or sintering process. The quantity of red mud is almost equal to the primary aluminium production: alkaline digestion of 2.5 T of bauxite produces 1 T of alumina and about 1.5 T of red mud [15]. The high alkaline content (pH > 11-13) of red mud and its enormous quantities caused significant ecological problems and considerable negative environmental effects [14]. Aluminium production in Hungary has been started from the thirties of the last century. From that time large amount of red mud has been accumulated and stored at different disposal sites in Hungary. There are ten cassettes near to Ajka plant operated by MAL Magyar Aluminium Co. Ltd. About 30 million cubic meters of red mud has been stored till October 2010 when the red mud catastrophe occurred. The slurry reservoirs covering 200 hectares in territory of the former Almásfüzitő alumina plant are located directly next to the Danube, containing 12 million T of waste in seven cassettes. 5 million T of red mud were accumulated in the reservoir behind the dam constructed in the valley of Kántorkerti stream near Neszmély, deposited by the Almásfüzitő alumina plant as well. The landfills of the Mosonmagyaróvár Alumina Plant, owned by MOTIM Ltd., are located at a few hundred kilometers from the city of Mosonmagyaróvár. The bauxite residues amounts to 3.7 T in terms of solid content. From disposal sites in Hungary the greatest environmental risk is posed by the Almásfüzitő facility in the direct vicinity of the Danube area. Out of the seven slurry basins located in that area, No. 7. cassette remains still partially uncovered, while the others are covered and recultivated. In average the solid content of stored bauxite residues at Hungarian sites is about 70% [5].

The main composition of red mud is summarized in Table 1. In addition to this the red mud contains valuable metals (Ga, Sc, Y, La, Ce, Pr, Nd, Sm, Cd, Mo, Zn, Cr, U, Th, Mn) and their concentration is about 1500-2000 ppm [3]. The red colour is caused by the oxidized iron, hematite mineral, present in an amount of 33-48 %. The red mud is not dangerous material itself. For the extraction of aluminium from bauxite ore sodium hydroxide (NaOH) is used with strong caustic character during the Bayer process. The caustic solution can make up to 70% of the mass of the red mud sludge and it is dangerous for environment. According to the Basel Convention of 1989 [1] (modified in 1998) on the control of transboundary movements of hazardous wastes and their disposal as well as the Hungarian Governmental Decree No. 240/2005 (X.27.) on the rules of the transboundary transportation of hazardous materials [2] the bauxite residue (red mud) with pH < 11.5 is considered to be non-hazardous. In case of the red mud waste disposal site close to Ajka the pH value of the red mud sludge was higher than 11.5, which exhibited danger for the environment and human health and should have been treated as hazardous waste [4].

Table 1. Red mud composition [3].

Main components	Amount, % (V/V)	Main components	Amount, % (V/V)
Fe_2O_3	33-48	P_2O_5	0.5-1.0
Al_2O_3	16-18	MgO	0.3-1.0
SiO_2	9-15	SO_3	0.4-0.8
Na_2O	8-12	CO_2	2-3
TiO_2	4-6	C	0.20-0.30
CaO	0.5-3.5	F	0.10-0.15
V_2O_5	0.2-0.3		

2. Description of the problems

Red mud is disposed as dry or semi dry material in red mud pond or abandoned bauxite mines and as slurry having a high solid concentration of 30-60% and with a high ionic strength. The environmental concerns relate to two aspects: very large quantity of the red mud generated and its causticity. Problems associated with the disposal of red mud waste include the following [11]:

- Its high pH (10.5-12.5);
- Alkali seepage into underground water;
- Alkaline air borne dust impact on plant life;
- Vast areas of land consumed;
- Instability of storage.

One the main reason of red mud catastrophe in Hungary was the instability of the storage reservoir. The rupture of the containment wall of the red mud storage facility at Ajka, Hungary in 2010 resulted in a very serious environmental disaster when about 1 million cubic meter of red mud sludge with a pH of 13 burst out of the waste disposal facility and flooded the neighbouring area with killing people and contaminating the surface waters and land (Fig.1).

Gypsum ($CaSO_4$) from power plant was used for the neutralization of the caustic solution of the spilled red mud. The neutralization step of red mud alkalinity can be represented by following main reaction [5].

$$CaSO_4 + 2\,NaOH \Leftrightarrow Ca(OH)_2 + Na_2SO_4$$

Figure 1. Red mud contaminated areas of Kolontár and Devecser villages in Central Transdanubia region of Hungary after the rupture of cassettes No 10 (waste reservoir) at waste red mud reservoir of MAL Co. Ltd. alumina plant in October 4th, 2010 [8].

After the catastrophe special attention was put onto the red mud disposal sites for preventing similar disaster. The safe disposal of the red mud is a must, however, since the red mud contains several valuable materials such as ferric, aluminium, titanium, silicon, calcium oxides and other metals e.g. germanium, gallium, etc. the recovery of the valuable components and the processing and utilization of the red mud considered as a secondary raw material are top issues and in this way the high environmental risk related to the storage can be mitigated.

The disposal and the utilization of red mud exhibit problem not only in Hungary, but in the majority of the European Union countries as well. For example Romania also has large amount of red mud disposed at different sites.

2. Discussion

2.1. Red mud disposal

Generally there are three ways of deposition of red mud: dumping into the sea, wet and dry disposals. In case of wet disposal the dry matter content is about 30% and remaining 70% is caustic solution with pH 12-13. In contrary to wet disposal the dry technique contains dry material in amount over 65% and caustic solution in amount less than 35% with pH 9-10 and the storage space requirement is less by 50-60% [10]. However, the main problem of the dry disposal is the formation of particulate matter (dust). Alkaline dust causes burning, respiratory tracts injuries and the extensive exposure may lead even to lung diseases. To avoid this problem the dry storage facility should be covered or top layer of dry red mud should be kept wet to prevent emission of the small particles.

During the past decades there is an increasing world tendency for the dry deposition of red mud against wet disposal and dumping it into the sea (Fig.2). Dry disposal of red mud was also considered by MAL Co. Ltd. company in the past, but it was required a significant investments and modernization of the technology.

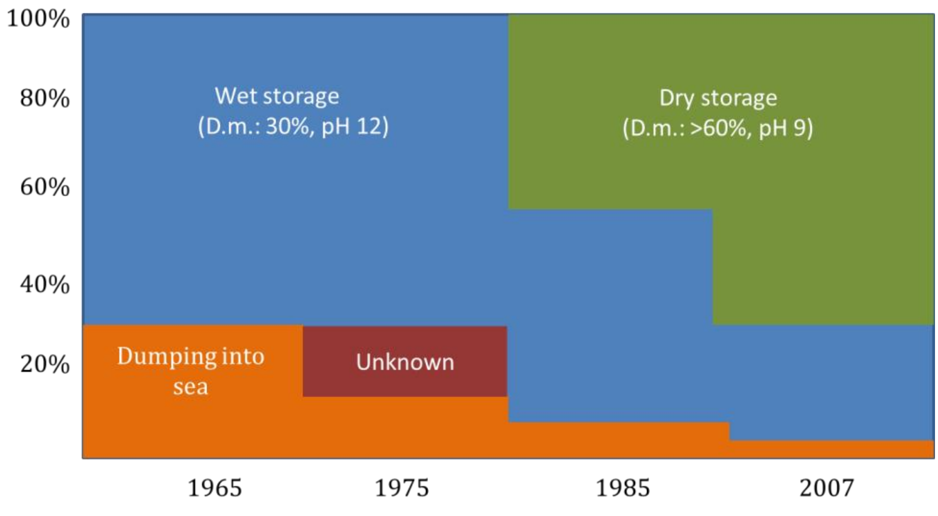

Figure 2. Data of red mud storage practices at 17 refineries representing 44% of global alumina production in 2007, where D.m.- dried matter [10].

After catastrophe the company was obliged to carry out modernization in the technology to make it safer for the environment. From February 2011 a new two-stage dry technology was applied at MAL Co. Ltd., which allowed decreasing the water content in slurry from 80% to 30%. In the first stage power plant gypsum was added to the filtered red mud having a dry material content of 55% formed on the existing drum filters in order to decrease the wet material content. In the second stage, the red mud formed on the drum filters having a dry material content of 55% is filtered by newly installed press filters to increase the dry material content to 65-70 %. This dry sludge is transported by lorries and is disposed at the storing area and does not require further drying for easy handling [5].

For a longer interim period gypsum will be added to the deposited sludge in order to condense it. This solution has not yet been used anywhere. As it has been mentioned above, its environmental impacts are unknown [5].

2.2. Utilization of red mud

Today the red mud is not used anywhere in Hungary. As it contains little aluminium oxide (15-19 %), its iron content is higher than that of bauxite, therefore, in principle, it could be used for iron production. Even though the manufacturing process is available in theory, it is nevertheless not used. The reason is that it is still significantly more expensive and energy intensive than producing iron from mined ores. Thus it is dumped as non-useful waste in reservoirs, and stored there until "better days" come [5].

It is a challenge for scientist and experts to devise profitable technologies and processes in order to produce valuable components/products from red mud, which is considered to be a hazardous waste if the pH value is high.

There are basically two main types of the processing and utilization of the red mud. The first one is its use as a uniform material for example for construction material manufacturing. The second possibility includes the separation of different components and transformation each of them into valuable products.

Concerning the options mentioned above reported on the utilization of red mud the use in building materials [13] such as cement [12], bricks, roof tiles and other ceramic products [9] should be emphasized. The incorporation of the red mud into these products could be beneficial in three ways. The bulk production of building materials could eliminate the disposal problem. Red mud will be considered as a raw material, added value would be given to it and the economic aspects regarding industrial implementation would be more favourable. Finally, this solution can be regarded therefore as an "easy to implement" and "broadly applicable" and it could be employed in several countries.

Cases have been reported on the successful recovery of major or minor constituents of the red mud, especially for metallurgical applications. For example the iron content can be separated by high gradient superconducting magnetic separation and then processed in the ferrous metallurgy [7]. However, it is not feasible up to now and the disposal problems for the remaining part of red mud still remain.

While searching for a way to produce higher-grade heating fuel from agricultural and forestry biomass, researchers at University of Guelph (Canada) recommend a technique that might make good use of red mud in the processing of bio-oil [6]. The high acidity of bio-oil makes it unstable, corrosive and very difficult to store. The tests carried out were successful in lowering the acid level of the organic liquid and producing higher-grade oil. The same process changes the red mud itself into a neutral magnetic material that is no longer caustic and toxic but that could be used as a building material.

The first step of utilization the of red mud should be started with neutralization of the caustic red mud followed by the utilization of the red mud e. g. for metal recovery, and use the valuable components as catalyst for different environmentally friendly technologies with or without combining with processing of other wastes/hazardous waste materials in order to produce products which could be marketed, and which are safe from environmental point of view.

3. Conclusions

In October 2010 an extremely serious environmental catastrophe occurred in Hungary since about of one million of cubic meter of red mud sludge burst out from the reservoir killing people and contaminating the surface waters and soil. This disaster focused the attention of the governmental people and scientists on the possibility of the processing and reutilization of the red mud.

These days the goal is the prevention of similar catastrophe by the continuous monitoring of the condition of red mud storage facilities/cassettes. Significant amount of red mud in past was deposited using wet storage technology. The scientists and experts aim at to find solutions for neutralization or removal of the caustic sodium hydroxide from the existing cassettes. Also work is going on the further development of dry storage technology to make it less dangerous for environment and human beings. To find safe and economically favourable way of utilization is a challenging task. Nowadays the attention is focused on iron and valuable metals extraction from the red mud.

It is to be noted that this problem is not a country specific problem. The majority of the EU countries experience the same problem from environmental point of view and there is an increasing pressure on the companies from the governmental administration and NGOs to comply with continuously tightening regulations. Therefore the development of new technologies including the neutralization of the caustic red mud, processing of the red mud, recovery of the precious metal components to manufacture products from a waste, or by combination of two hazardous waste materials have a tremendous importance. To solve this complex issue further research and international cooperation is necessary.

Acknowledgements

This work was supported by the European Union and co-financed by the European Social Fund in the frame of the TÁMOP-4.2.2/B-10/1-2010-0025 and TÁMOP-4.2.2.A-11/1/KONV-2012-0071 projects.

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