

Commentary

A review of the application of Bayer red mud in concrete

ABSTRACT: Bayer red mud is an industrial waste residue formed in the process of producing alumina by Bayer process in alumina plant. At present, the main disposal method of red mud is to send it to red mud dam for storage. Due to its high alkali content, it causes serious pollution to the surrounding environment and becomes an ecological problem to be solved urgently. In this paper, the application progress of Bayer red mud in concrete is summarized. This paper focuses on the possibility of red mud as a cementitious material, and deeply discusses the influence of red mud on the working performance and mechanical properties of concrete. Finally, the shortcomings in the current research of red mud concrete are pointed out, aiming to provide reference for the research direction of Bayer red mud in concrete.

Keywords: Bayer red mud ; resource utilization ; volcanic ash activity

1. INTRODUCTION

There are three commercially used processes for alumina refining, namely sintering process, Bayer process and combined process (Bayer-sintering). Before the 1990s, the sintering process was the only process used in China because of its high ratio of alumina extracted from lagoon bauxite. However, the energy consumption of the sintering process is much higher than the other two processes. In 1993, Shandong used the Bayer process to import Erjingtiao bauxite. High temperature Bayer process and flotation Bayer process have also been successfully applied to feldspar bauxite in China. At present, the sintering process is mainly used to produce chemical alumina. The sintering process is considered to be an important method for extracting alumina from low-grade bauxite, fly ash and other resources. However, these alternative methods are rarely used commercially in China. In 2011, sintering process alumina products accounted for about 2.5 % of total alumina production.

About 3 / 4 of China 's alumina production capacity is distributed in Henan, Shanxi, Guizhou, Guangxi, Yunnan and Chongqing, because these areas are rich in raspberry deposits. The remaining 1 / 4 of China 's alumina production capacity is located in Shandong Province because of its regional advantages in marine transportation of imported diabase. Most refineries have an annual alumina capacity of more than 1 million tons ^[1].

In the alumina production industry, Bayer red mud is produced as a waste by-product through the Bayer process. Bayer process is an industrial process for refining bauxite and producing alumina. This is widely used to produce alumina, which accounts for 95% of alumina production.

The raw bauxite and caustic soda were mixed together in the presence of lime, and the temperature of the mixture was maintained at about 100 °C to complete the pre-desilication stage. The bauxite was treated with a hot sodium hydroxide(NaOH) solution, so the alumina was converted into aluminum hydroxide $Al(OH)_3$. Other elements of the bauxite cannot be dissolved, so red mud will be formed after the solution is filtered [2].

In order to produce one ton of alumina, up to two tons of red mud will be produced. These solid mixtures are harmful to the environment due to their high alkalinity. It is reported that about 120 tons of red mud are produced every year in the world [3]. As the largest producer of alumina, China has 37.08 million tons of aluminum by 2020, resulting in a large amount of RM being discharged and hoarded. It takes up land, and the alkaline substances in RM can seriously pollute soil and water resources. Therefore, the effective utilization and environmentally sound treatment of RM has attracted much attention [4]. Due to the increasing demand for aluminum, this value will tend to increase in the next few years. This will also increase the resulting red mud. The main red mud treatment methods currently used around the world are marine discharges, lagoons and dry piles. The greatest impact on the environment of red mud disposal and storage is the soil and water pollution caused by residual suspension. The environmental risk mainly depends on the amount of suspension in the slurry and the possibility of interaction between the slurry and environmental components [5]. Red mud is disposed of in landfills and stored for long periods in large lagoon-type reservoirs. It poses a threat to the environment and is economically unsustainable due to increasing consolidation. There is an urgent need to develop new and improved technologies to properly store and dispose of these wastes.

The research on red mud concrete was searched in Web of Science. Figure 2 shows the number of papers published from 2011 to 2022, which shows the utilization trend of red mud in recent years. In recent years, the number of articles published each year has increased from a small number of articles in 12 years to more than 2022 times. This shows that the application of red mud in concrete has been further developed.

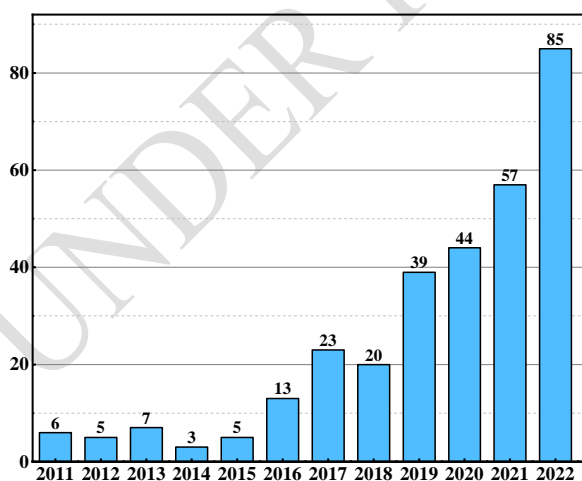


Fig. 1. Number of articles on red mud published by WoS from 2011 to 2022

Figure 2 shows the statistical data of effective utilization of red mud in various civil engineering applications around the world. It can be seen from the figure that the utilization rate of red mud in China is not particularly low, but because the amount of red mud produced in China is too large, new methods need to be found to use or deal with it.

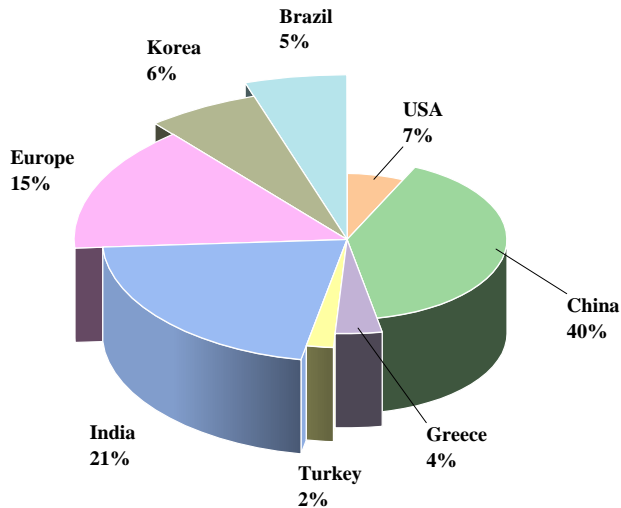


Fig. 2. Statistics of red mud research in the world [6]

2. RED MUD

2.1 BASIC CHARACTERISTICS OF BAYER RED MUD

2.1.1 Formation process

The Bayer process is to grind the bauxite to the required particle size, add caustic soda lime under high temperature and high pressure conditions, and obtain a sodium aluminate solution through a series of reactions. After entering the cooling device, the sodium aluminate is diluted with water. After hydrolysis, $\text{Al}(\text{OH})_3$ is generated, and a solution containing a large amount of NaOH is obtained. After evaporation and concentration, it is returned to dissolve a new batch of bauxite to achieve continuous production. $\text{Al}(\text{OH})_3$ can be decomposed into Al_2O_3 after high temperature calcination. The substance that does not react with NaOH during the reaction will form a solid precipitate and be filtered out, and the formed filter residue is red. This substance is Bayer red mud.

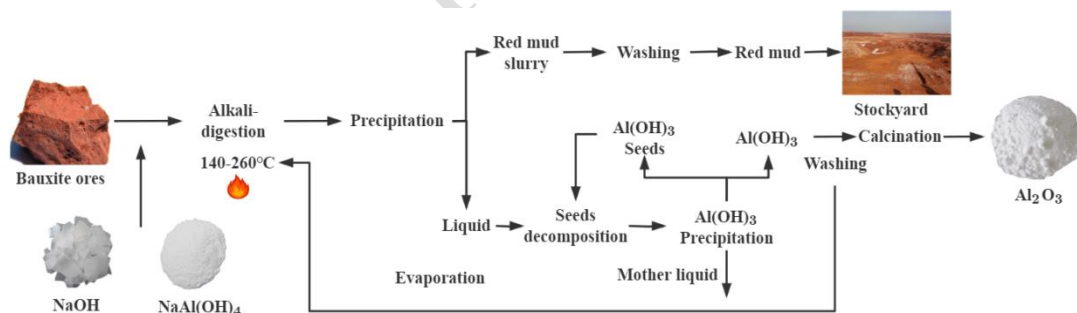


Fig. 3. Simplified process diagram of Bayer process [7]

2.1.2 Appearance and microstructure

The morphology of the two red mud powders is shown in Figure 4 and Figure 5. Sintered RM is dark yellow, while Bayer RM is crimson. It is found by microscope that red mud is composed of fine particles, and the particle size varies from a few microns to dozens of microns. Red mud is characterized by irregular shapes, including flake and spherical particles. Usually, due to agglomeration, large aggregates are composed of much smaller particles. The particles were identified as amorphous (poorly crystallized), relatively dispersed and disordered. Due to particle agglomeration, there is a gap between fine particles.

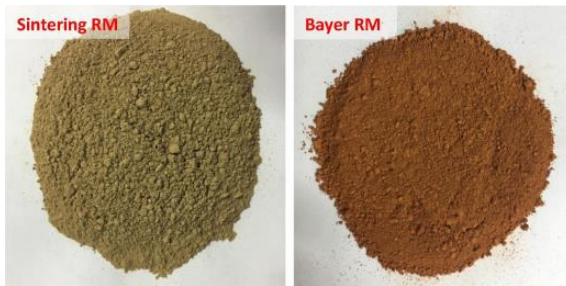


Fig. 4. The morphology of two kinds of red mud produced by sintering process and Bayer process [8]

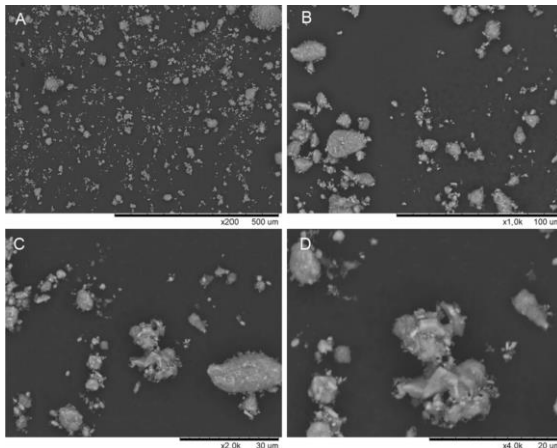


Fig. 5. SEM of RM at four magnifications : (A) × 200; (B) × 1000; (C) × 2000; (D) × 4000 [9]

2.2 UTILIZATION OF RED MUD

Nowadays, the utilization of red mud is more extensive. Although the strength of red mud is not as strong as other commonly used solid waste in construction, the scope of application is gradually increasing. The red mud produced by sintering and combination process can be used to produce building materials and glass ceramics. High-iron red mud can use certain technical means to separate iron. Not only that, red mud contains many other trace elements, which can be extracted for other purposes.

Compared with alkali reactive materials such as GBFS and FA, the gelling active potential of RM is difficult to be highly excited. Reducing the particle size of RM by mechanical grinding and increasing the specific surface area can stimulate its activity to a certain extent, but the activity of this method is not high, and excessive grinding will also cause the agglomeration of RM particles. For Bayer RM, the main activation method is high temperature calcination, and the huge energy consumption is obviously unrealistic for large-scale utilization [10].

3. PROCESSING METHOD TO IMPROVE THE REACTIVITY OF RED MUD

Red mud is highly alkaline and composed of aluminosilicate, which makes it a potential source material for concrete. In order to obtain higher strength, additional alkali solutions, such as NaOH and sodium silicate, are required. Due to poor activity and low $\text{SiO}_2/\text{Al}_2\text{O}_3$ (less than 2), the raw materials received do not have the activity to participate in the reaction. It requires fine grinding and thermal pre-activation, or calcination at temperatures up to 800-900 °C [11], or mixing with other materials with activated SiO_2 to improve the reactivity of the material [12].

3.1 HEAT TREATMENT

Venkatash et al [13] heat-treated the red mud at 600 °C for 2h, and analyzed the chemical composition of the treated and untreated red mud by XRF. The results are shown in Table 1.

Table 1. Chemical Composition of Treated and Untreated Red Mud

	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	MgO
Untreated red mud	5.9	21.37	20.97	14.98	12.87	10.12	0.39
Treated red mud	4.9	23.79	28.24	19.90	7.5	10.83	0.39

Nath et al ^[14] studied the phase composition and structural transformation of RM fluid at different temperatures. The peak of the sample treated at 500 °C showed that there was no gibbsite. This is because gibbsite is decomposed into Al₂O₃ and H₂O according to the following reactions, which can also explain the increase of Al₂O₃ in red mud after heating treatment in the above table.

Literature ^[15] showed that the above transformation occurred at temperatures above 600 °C. However, in this study, it was found that the above conversion occurred at 500 °C, which may be due to the proper heating of RM samples in a fluidized bed reactor.

In the experiment of Zhu et al ^[16], a new mineral composition of NaOH-H₂O and Na₂Ca(CO₃)₂ appeared at 700 °C, and the diffraction peak of Na₆CaAl₆Si₆(CO₃)O₂⁺ 2H₂O disappeared. However, new mineral compositions of Ca₂Al₂SiO₇ and Ca₃Si₂O₇ appeared at 900 °C, and the peaks of NaOH-H₂O and Na₂Ca(CO₃)₂ decreased. ◦

3.2 GRIND

In the experiment of Singh et al ^[17], lime reactivity test was carried out on the ground red mud to evaluate the zeolite behavior of raw materials. The test results show that red mud is almost non-boiling in nature. The particle size of all phases of the processed red mud decreases, and the lime reactivity value increases. The percentage of active silicon in red mud also increased from 1.62 to 5.12 after crushing.

Li et al ^[18] found that the hydration process was slightly delayed when ultrafine red mud was used in the slurry. In addition, when the content of ultra-fine red mud increases to 70 wt %, the hydration reaction rate decreases sharply. This is because when the amount of ultra-fine red mud is too much, its morphology effect and micro-aggregate effect decrease, and the effect of low cement-based reactivity on hydration reaction is more significant. Coarse red mud significantly delayed the hydration process due to its low cementitious reactivity, and mechanical activation enhanced the cementitious reactivity of red mud.

4. THE PERFORMANCE OF CONCRETE MIXED WITH BAYER RED MUD AS CEMENTITIOUS MATERIAL

4.1 FLUIDITY

Ma et al ^[19] used red mud instead of dead burned magnesium oxide(MgO) to study its effect on the setting time and fluidity of the slurry. The test shows that the setting time of the slurry gradually increases with the increase of red mud content. This is because the addition of red mud reduces the content of MgO in the slurry, and the reactivity of red mud is lower than that of MgO, so the acid-base reaction rate is delayed and the setting time is increased. When the amount of red mud is 20%, the fluidity of the fresh slurry increases from 210 mm to about 240 mm, but when the amount of red mud is 40%, the fluidity decreases significantly. This shows that an appropriate amount of red mud can effectively improve the fluidity of fresh slurry. Compared with MgO, the overall particle size of red mud is smaller. An appropriate amount of red mud can optimize the particle size distribution of raw materials and improve the fluidity. However, finer particles and larger specific surface area also mean that red mud will absorb more water, and when the content of red mud is too high, it will lead to a decrease in fluidity.

4.2 COMPRESSIVE STRENGTH

Song et al ^[20] used Bayer red mud instead of fly ash to prepare autoclaved aerated concrete, and studied its influence on the workability and mechanical properties of concrete. The results show that the fluidity and compressive strength decrease linearly with the increase of red mud content.

Viyasun et al ^[21] replaced cement with red mud at a replacement rate of 10%, 20%, and 30%, respectively, and compared the average compressive strength of concrete partially replaced by different percentages of red mud with traditional concrete values. It can be seen that the compressive strength value of red mud partially replacing 20% concrete is greater than that of conventional concrete. This is because the pressure mass and the adhesion between cement and aggregate increase. The further increase in the percentage of red mud in concrete did not show any increase in compressive strength. Compared with the former, the bond contribution between cement and aggregate was smaller. The concrete sample with 20 % red mud has better tensile value than other samples. The increase of red mud percentage by more than 20 % will lead to a decrease in the tensile value.

Chavan et al ^[22] replaced part of the cement with red mud and carried out bending, compression and splitting tensile strength tests. The results show that the compressive strength, flexural strength and splitting tensile strength of red mud instead of cement are on the rise, up to 12%. After the substitution level of 12%, the mechanical properties decrease. When red mud replaces 12 % of cement, the compressive strength, splitting tensile strength and bending strength are the largest. This is because 12% of cement replaces red mud to enhance the internal microstructure of concrete, resulting in the best, denser and less void morphology.

4.3 DURABILITY

4.3.1 modulus of elasticity

Ghalehnovi et al ^[23] studied several mixtures containing RM as partial cement and filler substitutes. The elastic modulus value decreased with the increase of RM content, and the control group was the highest. According to the study of Davraz et al ^[24], variables such as the elastic modulus of the cement matrix, the type and content of the aggregate, the W/C ratio, and the volume of the bonding material will significantly affect the elastic modulus of the concrete. Therefore, when RM is used in series concrete, the decreasing trend of its performance may be related to its low zeolite activity, because it constitutes a considerable part of the binder.

4.3.2 resistance to chloride ion penetration

Chavan ^[25] conducted chloride permeability (RCPT) tests by partially replacing cement with different proportions. The results show that the control concrete prepared with 0% red mud shows the largest chloride permeability value. When red mud (RM) replaces less than 12% of cement, the chloride permeability value shows a downward trend. This is because when red mud replaces cement by 12%, it provides the best mix of microstructures with smaller porosity, denser, and better distribution, resulting in higher density, better fillers, and fewer voids ^[26]. Because RM is alkaline, its presence in concrete enhances resistance to chloride ion penetration, thereby reducing the total charge passed through. Therefore, replacing cement with RM in concrete will reduce the charge passed through, which further indicates the resistance to chloride ion penetration.

5. CONCLUSION

The effect of RM on cement-based composites is highly related to its chemical and physical

properties, and changes with the formation process of alumina. Although differences between early compressive strength results can be seen in most of the literature, studies have shown that RM can improve mechanical properties at later ages. In addition, the use of a sufficient amount of RM helps to form a denser structure, the total porosity is reduced, and the pores are smaller. On the contrary, RM is most likely to reduce the fresh mixing performance, because it has a significantly larger specific surface area (about 20 times) than cement, which is due to the presence of porous hornfels in its structure. RM reduces processability and increases initial and final setting time due to the presence of aluminum and sodium hydroxide. When used in high content, it will reduce the maximum temperature in the hydration process, but will not significantly change the hydration process.

REFERENCES

- [1] W. Liu, X. Chen, W. Li, Y. Yu, K. Yan, Environmental assessment, management and utilization of red mud in China, *Journal of Cleaner Production*. 2014;84: 606-610.
- [2] M.A. Khairul, J. Zanganeh, B. Moghtaderi, The composition, recycling and utilisation of Bayer red mud, *Resources, Conservation and Recycling*. 2019;141:483-498.
- [3] S. Vigneshwaran, M. Uthayakumar, V. Arumugaprabu, Development and sustainability of industrial waste-based red mud hybrid composites, *Journal of Cleaner Production*. 2019;230: 862-868.
- [4] K. Chen, W.-T. Lin, Q. Liu, B. Chen, V.W.Y. Tam, Micro-characterizations and geopolymerization mechanism of ternary cementless composite with reactive ultra-fine fly ash, red mud and recycled powder, *Construction and Building Materials*. 2022;343:128091.
- [5] W.C. Tang, Z. Wang, Y. Liu, H.Z. Cui, Influence of red mud on fresh and hardened properties of self-compacting concrete, *Construction and Building Materials*. 2018;178:288-300.
- [6] M. Muraleedharan, Y. Nadir, Factors affecting the mechanical properties and microstructure of geopolymers from red mud and granite waste powder: A review, *Ceramics International*. 2021;47 (10, Part A):13257-13279.
- [7] S.M.A. Qaidi, B.A. Tayeh, H.U. Ahmed, W. Emad, A review of the sustainable utilisation of red mud and fly ash for the production of geopolymer composites, *Construction and Building Materials*. 2022;350:128892.
- [8] J. Zhang, S. Liu, Z. Yao, S. Wu, H. Jiang, M. Liang, Y. Qiao, Environmental aspects and pavement properties of red mud waste as the replacement of mineral filler in asphalt mixture, *Construction and Building Materials*. 2018;180:605-613.
- [9] M. Lorena Figueiredo Martins, P. Roberto Ribeiro Soares Junior, T. Henrique da Silva, P. de Souza Maciel, I. Peixoto Pinheiro, A. Cesar da Silva Bezerra, Magnesium industry waste and red mud to eco-friendly ternary binder: Producing more sustainable cementitious materials, *Construction and Building Materials*. 2021;310:125172.
- [10] J. Xu, F. Xu, Y. Wu, Y. Liu, F. Yang, Y. Jiao, Y. Jiang, J. Zhu, S. Li, D. Wang, B. Li, Investigation on properties and mechanism of non-calcined Bayer red mud-phosphogypsum cementitious binder, *Journal of Cleaner Production*. 2022;379:134661.
- [11] E.P. Manfroí, M. Cheriaf, J.C. Rocha, Microstructure, mineralogy and environmental evaluation of cementitious composites produced with red mud waste, *Construction and Building Materials*. 2014;67:29-36.
- [12] V.Q. Le, M.Q. Do, M.D. Hoang, T.P. Dang, T.H. Bui, H.T. Nguyen, Evaluation on

Roles of Activated Silicon and Aluminum Oxides for Formation of Geopolymer from Red Mud and Silica Fume, *Key Engineering Materials*. 2018;777:513-517.

[13] C. Venkatesh, R. Nerella, M. Sri Rama Chand, Comparison of mechanical and durability properties of treated and untreated red mud concrete, *Materials Today: Proceedings*. 2020;27:284-287.

[14] H. Nath, P. Sahoo, A. Sahoo, Characterization of Red Mud treated under high temperature fluidization, *Powder Technology*. 2015;269:233-239.

[15] C.-s. Wu, D.-y. Liu, Mineral Phase and Physical Properties of Red Mud Calcined at Different Temperatures, *Journal of Nanomaterials*. 2012;2012:628592.

[16] X. Zhu, W. Li, X. Guan, An active dealkalization of red mud with roasting and water leaching, *Journal of Hazardous Materials*. 2015;286:85-91.

[17] S. Singh, M.U. Aswath, R.V. Ranganath, Effect of mechanical activation of red mud on the strength of geopolymer binder, *Construction and Building Materials*. 2018;177:91-101.

[18] Z. Li, H. You, Y. Gao, C. Wang, J. Zhang, Effect of ultrafine red mud on the workability and microstructure of blast furnace slag-red mud based geopolymeric grouts, *Powder Technology*. 2021;392:610-618.

[19] S. Ma, Z. Zhang, X. Liu, Y. Li, Q. Zeng, W. Zhang, Reuse of red mud in magnesium potassium phosphate cement: Reaction mechanism and performance optimization, *Journal of Building Engineering*. 2022;61:105290.

[20] Y. Song, M. Dong, Z. Wang, X. Qian, D. Yan, S. Shen, L. Zhang, G. Sun, J. Lai, S. Ruan, Effects of red mud on workability and mechanical properties of autoclaved aerated concrete (AAC), *Journal of Building Engineering*. 2022;61:105238.

[21] K. Viyasun, R. Anuradha, K. Thangapandi, D. Santhosh Kumar, A. Sivakrishna, R. Gobinath, Investigation on performance of red mud based concrete, *Materials Today: Proceedings*. 2021;39:796-799.

[22] S.P. Chavan, S.A. Salokhe, P.A. Nadagauda, S.T. Patil, K.M. Mane, An investigational study on properties of concrete produced with industrial waste red mud, *Materials Today: Proceedings*. 2021;42:733-738.

[23] M. Ghalehnovi, E. Asadi Shamsabadi, A. Khodabakhshian, F. Sourmeh, J. de Brito, Self-compacting architectural concrete production using red mud, *Construction and Building Materials*. 2019;226:418-427.

[24] M. Davraz, H. Ceylan, İ.B. Topçu, T. Uygunoğlu, Pozzolanic effect of andesite waste powder on mechanical properties of high strength concrete, *Construction and Building Materials*. 2018;165: 494-503.

[25] S.P. Chavan, S.A. Salokhe, P.A. Nadagauda, S.T. Patil, K.M. Mane, An investigational study on properties of concrete produced with industrial waste red mud, *Materials Today: Proceedings*. 2021;42:733-738.

[26] K. Hyeok-Jung, S.-P. Kang, G.-C. Choe, Effect of Red Mud Content on Strength and Efflorescence in Pavement using Alkali-Activated Slag Cement, *International Journal of Concrete Structures and Materials*. 2018;12 (1): 18.