Journal of Non-Crystalline Solids 475 (2017) 129–135

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Vitrification of red mud with mine wastes through melting and granulation process – Preparation of glass ball

Hyun Sik Park[a], Joo Hyun Park[b,*]

[a] Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 34132, Republic of Korea
[b] Department of Materials Engineering, Hanyang University, Ansan 15588, Republic of Korea

ARTICLE INFO

Keywords:
Vitrification
Red mud
Gold tailing
Waste limestone
Heavy metals
Glass ball

ABSTRACT

Concentrated radioactive elements and high alkalinity prevent the general usage of red mud to the glass-ceramics and construction materials. Gold tailing has inadequate particle sizes (≤ 100 μm) for use in ceramic industry, and waste limestone contains lime of too low quantity. Hence, the combinatorial design for the utilization of these industrial wastes was investigated to obtain functional and environmentally stabilized glass ball. Red mud (RM) was vitrified by melting and granulation process with addition of gold tailing (GT) and waste limestone (WL). The mass ratio between raw materials (RM:GT:WL = 1:1:1) and the viscosity of the glass melts (1.5 Pa·s) were optimized for the melting and granulation process. From gamma spectroscopy, the radioactive nuclide concentration in the granulated glass ball was significantly decreased. Also, the granulated glass balls showed excellent resistance against leaching of heavy metal ions based on the results of the toxicity characteristic leaching procedure (TCLP).

1. Introduction

Mass production of aluminum was facilitated by the introduction of the Bayer process and Hall-Héroult process in the late 19th century. Bauxite ore is first purified to alumina, which is then smelted in molten cryolite by electrolysis to produce aluminum metal. The important feature exploited in the Bayer process is that alumina can be dissolved in sodium hydroxide solutions under moderate conditions, while other components are inert in the process [1]. During this process, a large quantity of residue is generated after washing and is very alkaline and could contaminate ground water. The well-known name red mud for this bauxite residue is due to the large amount of hematite present in the residue.

During the nearly 120 years of alumina extraction from bauxite, this residue has been problematic; however, there has been no successful resolution [1]. This bauxite residue issue can be classified into two categories of appropriate disposal and moderate utilization [2,3]. The methods used for disposal have improved over time and include marine discharge, lagooning, dry staking, and various remediation techniques [2]. According to Power et al. [2], the alkalinity of bauxite residue is the most important barrier to remediation and utilization. A variety of technologies already exist to fully utilize bauxite residue, including those in the areas of construction and chemical applications, environmental and agronomic application, and metallurgical application [3]. However, no significant use of bauxite residue has been reported despite over 50 years of research and technological development, mainly due to the associated cost and risk [3].

On the other hand, mineral wastes consisting of waste rock and tailings are also a potential risk to the environment. Gold tailing discharged after the floatation process can contain residual cyanides [4,5], arsenide [6], or mercury [7], which accumulate near the operating plants and can be released to the surrounding environment during a dam failure, as has been reported in history [8]. Impoundment or dry staking of tailing are known to be vulnerable to scattering of mineral particles and distribution by rainwater [5]. Small particle size under 100 μm and high quartz content (≥ 87%) limit the direct usage of gold tailings in construction materials. Additional treatment such as firing, cementing, or geo-polymerization are required to produce bricks or aggregates [9]. However, hazardous components of tailing are not stabilized by sintering and can be released depending on external circumstances.

Lastly, waste limestone is another important issue for miners. A significant amount of waste limestone of low quality (≤ 40%) is generated during the mining process and does not have economic value for the cement or steel industries. Partial replacement of sand powder with this limestone in the concrete process has been reported [10], but the substitution rate is limited. Near a limestone quarry, soil and underground water contamination are highly expected due to the heavy

---

* Corresponding author.
E-mail address: basicity@hanyang.ac.kr (J.H. Park).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.010
Received 17 June 2017; Received in revised form 19 August 2017; Accepted 1 September 2017

metals present.

As individual materials, red mud, gold tailing and waste limestone cannot be vitrified or used for valued products. However, the treatment of these industrial wastes using pyrometallurgical methods may provide the ideal solution for mass consumption with additional economic and environmental benefits [11]. The major components of red mud, gold tailing, and waste limestone are hematite, alumina, quartz, and lime. Four oxides (Fe_2O_3, Al_2O_3, SiO_2, and CaO) constitute most of the ironmaking and steelmaking slags of the ferrous industry [12,13]. Since the thermophysical properties and the refining capabilities of the ferrous slag systems have extensively been studied for the past century [14], existing thermodynamic data in the literature and software can be easily used. Possible combinations of oxides and their optimal melting conditions can be simulated accordingly [14,15].

Granulation of molten oxides has been recently employed by steelmaker and non-ferrous smelters [16]. Air blasting and water granulation are typical methods to process huge quantities of waste slags. Many research attempts have focused on energy recovery from the waste heat of molten slags [16]. Industrial trials as well as a laboratory scale investigation by Japanese researchers have received much attention due to the CO_2 emissions and energy reduction issues [17–20]. Commonwealth scientific and industrial research organization (CSIRO) of Australia recently developed the dry slag granulation technique with improved heat recovery and is ready for industrial application [21]. Granulated slags have versatile uses as abrasives, concrete mixer, aggregates, and pavements. The sales price varies depending on particle size and physicochemical properties of granules.

This study investigated the vitrification of red mud using gold tailing and waste limestone as flux materials. The mass ratio of raw materials for melting and granulation was determined from thermodynamic calculations by FactSage™7.0, which is a commercial thermochemical computing package [22]. Considering the main components of the industrial wastes, the CaO-FeO_x-Al_2O_3-SiO_2 quaternary oxide system was used to identify mixing conditions. Different mass ratios of red mud, gold tailing, and waste limestone were tested to find the optimum composition for glass ball production. High-temperature melting was conducted at 1773 K, followed by granulation by air blowing. Granules were evaluated by size distribution and average sphericity. High production yield and improved sphericity of glass balls showed the potential for commercial grade production.

Vitreous products made of potential hazardous industrial wastes were tested for radioactivity and chemical stability. The radioactive nuclide concentration of granules was significantly decreased, and the diluted result of radioactive elements (U, Th) was confirmed. The granulated balls showed excellent resistance against leaching of heavy metal ions (Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}) based on the results of the toxicity characteristic leaching procedure (TCLP).

2. Materials and methods

2.1. Raw materials

Red mud used for the current study was obtained from a local Bayer process (KC Corporation, South Korea). Limestone from the cement industry (Korea Cement, South Korea) and gold tailing supplied by a regional gold mine (Golden Sun Inc., South Korea) were used as flux materials for high-temperature experiments. Quantitative compositional analysis was conducted by X-ray florescence (XRF) spectrometry (XRF-1800, Shimadzu, Kyoto, Japan) as shown in Table 1. Red mud is mainly comprised of hematite and alumina, while silica constitutes most of the composition of gold tailing. Calcium oxide is a major component of waste limestone that loses 35% of its mass during calcination. The dominant phases in raw materials were analyzed by powder X-ray diffraction (XRD, D/Max 2200, Rigaku, Tokyo, Japan). The XRD patterns were obtained by recording the characteristic diffraction intensities with a nickel filtered Cu *K*α-radiation set at 40 kV, 30 mA, and a two theta range from 10 to 80 using a step size of 0.033 degrees. The major peaks of the RM, GT, and WL are shown in Fig. 1. Hematite and boehmite (aluminum hydroxide) are the dominant phases in the red mud. Quartz is the main phase of gold tailing. Calcite is the major phase of WL according to the XRD patterns.

Table 1
Quantitative compositional analysis of raw materials by XRF (wt%).

	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	MgO	K_2O	Ignition loss
RM	30.8	24.8	12.4	4.3	8.6	6.7	–	–	12.4
GT	1.1	6.0	87.7	0.1	0.3	0.2	0.1	1.3	3.2
WL	0.9	2.2	12.4	42.6	–	0.1	2.6	0.9	35.3

As shown in Table 2, radioactive elements (U, Th) were analyzed by high-resolution inductively coupled plasma – mass spectrometry (ICP-MS, ELAN DRC II, Perkin Elmer, NY, USA). Nuclide concentrations evaluated by Ra-226, Th-232, and K-40 were measured using the standard test method for nondestructive analysis of special nuclear materials in homogeneous solutions by gamma-ray spectrometry [23]. Heavy metals contained in the raw materials were analyzed by inductively coupled plasma – optical emission spectroscopy (ICP-OES, 5300DV, Perkin Elmer, NY, USA), as shown in Table 3, including the amounts of Cr, Cu, and Pb in ppm. Cadmium (Cd) was analyzed by high-resolution inductively coupled plasma – mass spectrometry (ICP-MS, ELAN DRC II, Perkin Elmer, NY, USA) due to detection limit of ICP-OES. Triplicated samples were used for the ICP-OES and ICP-MS to minimize the uncertainties of measurements.

2.2. Experimental methods

Moisture in the powders was removed by drying at 473 K for 24 h before use. Fine particles sized under 100 μm were sieved for pelletization. Raw materials were mixed in a rotating drum for 24 h to obtain homogeneity. Mixed powers were agitated in a stirring mixer with addition of distilled water to supply adequate moisture to the paste mixture. Samples were pelletized by hand rolling to produce the desired spherical shape with 50 mm diameter. Pellets were dried at 474 K for 7 days to eliminate the residual moisture.

The oxide system corresponding to the major components of red mud, gold tailing, and limestone was designed based on the CaO-FeO_x-Al_2O_3-SiO_2 quaternary system [14]. Oxide compositions with a low melting point were selected to ensure low heat energy consumption of the granulation process. Fig. 2 shows the liquidus isotherm of 1573 K in the polythermal projection of the CaO-10%FeO_x-Al_2O_3-SiO_2 pseudo-ternary phase diagram. In the present sample preparation, the redox-equilibrium reaction of iron oxide in the CaO-10%FeO_x-Al_2O_3-SiO_2 pseudo-ternary system redistributes the Fe^{2+}/Fe^{3+} ratio of the Fe_2O_3 contained mainly in the red mud. Wüstite-based compounds will appear depending on the basicity (CaO/SiO_2 mass ratio) in the partially liquid phase.

Compositions of samples mixed according to mass ratio of red mud (RM), gold tailing (GT), and waste limestone (WL) are shown in Table 4. Mixing ratios (RM:GT:WL) of 1:2:1, 1:1:1, and 1:1:2 by mass were selected to simplify raw material preparation. The basicity, which impacts the physicochemical properties of the melts, was described as the mass ratio between CaO and SiO_2. Amphoteric oxides such as Al_2O_3 and FeO_x were assumed to behave as neutral to the basicity. The compositions of samples A, B, and C are roughly illustrated in the phase diagram in Fig. 2. Despite some errors due to the minor elements, the basicity of the melt could be controlled in the range from about 0.3 to 1.0 by changing the mixing ratio.

A schematic of the melting and granulation process is shown in Fig. 3. Dried pellets 50 mm in diameter were introduced into a pure grade (99.9%) cylindrical graphite crucible with one liter capacity. For each trial, 12 pellets weighing 70 to 80 g in total were used. A high-