Journal of Environmental Chemical Engineering 4 (2016) 3065–3074

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Green process for supercritical water oxidation of sewage sludge with red mud as CO_2 absorbent

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ARTICLE INFO

Article history:
Received 3 April 2016
Received in revised form 22 May 2016
Accepted 10 June 2016
Available online 17 June 2016

Keywords:
Sewage sludge
SCWO
Red mud
CO_2 mineralization

ABSTRACT

To mineralize CO_2 produced in situ and other acidic substances originating from organic components in sewage sludge, we developed a green SCWO system involving the treatment of sewage sludge with red mud as an alkaline absorbent. In this new system, two steps of mineralization were covered. Primary mineralization occurred inside the SCWO reaction vessels with part of CO_2 produced in situ. By this primary treatment, total inorganic carbon of the solid residue increased rapidly, predominantly in the form of calcite. Moreover, the S and P content increased by more than ten times compared with that of pure sludge. The pH of the drained water increased from 5.16 to about 7.7 with the addition of 2% red mud. The second mineralization step involved the exhausts cleaning reaction using red mud slurry. With 2.5 h of cleaning reactions at pressures of 0.1, 1, 3, and 5 MPa, approximately 4.49, 5.30, 6.06, and 7.52 g, respectively, of CO_2 per 100 g of red mud were bound in calcite. The high CO_2 absorption capacity was ascribed to the high pressure cleaning reaction, which was conveniently achieved in this SCWO system just by a simple adjustment of the back-pressure valve. With this green SCWO disposal, CO_2 level in the exhausts were cut to below 800 ppm (mg/L); SO_2 and nitrogen oxides (NO, NO_2) diminished to below 15 ppm and 12 ppm, respectively. Due to the comparative stability of the solid residues obtained, they can easily be handled using conventional methods or recycled for a range of industrial applications including building materials, water treatment materials, special ceramics, or silicate cements.

1. Introduction

There has been a significant global increase in sewage sludge due to the upgrade and expansion of wastewater treatment plants demanded by the wide range of industrialization and urbanization. This has become an important environmental concern, especially in some developing countries [1,2]. Incineration [3,4] or co-incineration [5,6] was considered a satisfactory disposal option for sewage sludge not long ago. However, many individuals and organizations, are now concerned about the potential long-term risks of related gaseous emissions of toxic compounds (e.g., dioxins) [7–9] and large amounts of greenhouse gases (GHG, e.g., carbon dioxide) [10,11]. For these reasons, there is an urgent need to develop new, appropriate disposal techniques for sewage sludge, with large treatment capacity and no gaseous emission.

Supercritical water oxidation (SCWO) disposal of sewage sludge presents a more effective means of avoiding toxic emission owing to the overwhelming destruction of organic compounds in a supercritical water medium [12–14]. The water becomes a non-polar solvent above its critical point ($T > 374\,^{\circ}C$, $P > 22.1$ MPa). In this condition, it is able to dissolve a wide range of substances including most organic compounds and light gases, although they are insoluble in ambient water [15,16]. Therefore, problematic organic pollutants are oxidized in a homogenized fluid phase, with the constituent carbon atoms being completely oxidized to CO_2; the hetero-atoms including sulfur, chloride, and phosphorus, are eventually converted to their corresponding inorganic acids [17]. Many investigations have demonstrated that SCWO is a preferable disposal route for various types of sludge, with excellent COD removal efficiency ($\geq$99%) [18–20]. However, if the large amounts

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http://dx.doi.org/10.1016/j.jece.2016.06.013
2213-3437/

of gaseous emission resulting from oxidation of organic components in sludge are emitted freely regardless of its potential hazard, it would add another challenge to environmental conservation and sustainable development in the future [21,22]. Therefore, GHG emission-free SCWO disposal, especially regarding CO_2 emission, has become more and more attractive.

Considering the remote locations of many sewage sludge treatment plants, directly sequestering the CO_2 produced in situ, may work better than purifying and using it. To date, the available methods for CO_2 capture and sequestration include geological sequestration [23], physical [24] and chemical [25] absorption, membrane separation [26], cryogenic distillation [27] and mineralization processes [28,29]. Among these methods, mineral carbonation is the most promising one because it results in permanent storage of CO_2 in the form of mineral carbonates that are environmentally benign and stable.

Each year, more than 70 million tons of a hazardous waste from the industrial production of aluminum known as red mud, is produced during the Bayer processing of bauxite [30–32]. Due to its high alkalinity (pH 13), which is associated with its composition of oxides of alkali metals and alkaline-earth metals, red mud has been reported to be an inexpensive and effective alkaline adsorbent [33–35]. Using red mud to simultaneously mineralize the CO_2 produced in situ, and other acidic substances, during the SCWO disposal of sewage sludge seems very attractive. Not only would it be free from GHG emission, but it would also eliminate environmental concerns related to storage of red mud, which is regarded as a risk to all nearby living organisms [36].

The purpose of this work was to develop a process for green SCWO disposal of sewage sludge, with simultaneous mineralization of acidic substances, using red mud. In this new system, part of the red mud was introduced into the SCWO reaction vessels by mixing it with sludge. This was to mineralize the CO_2 produced in situ, along with other acidic substances closely related to the corrosion of vessels and pipelines. Another part of the red mud was made into slurry and enclosed in an exhaust cleaning vessel connected with the SCWO set up. All of the exhaust gases from the gas-liquid separator were cleaned using the red mud slurry, before being released into the ambient air. With this green SCWO route, the majority of the acidic substances produced in situ were neutralized and converted to innocuous solid minerals such as calcite, which resulted in very low GHG emissions. Furthermore, due to the mineralization reactions, the solid residues obtained were relative stable, which makes relatively easy post-disposal or recycling possible.

2. Materials and methods

2.1. Sewage sludge

The active sewage sludge used in this work was supplied by Xiao Jiahe Wastewater Treatment Plant, Chongqing, China. Its water content was 95.5%, which was determined by measuring the weight loss before and after it was dried at 105 °C for 8 h. Total carbon (TC) of the dried sludge was 123,500 mg/kg, with a total inorganic carbon (TIC) proportion (TIC/TC) of 16.60%. This was determined using an Analytic Jena multi N/C 3100 Analyzer (Germany). During the measurement of carbon content, an oxygen gas was used as the burning gas and a helium gas was used as the carrier gas to provide an inert atmosphere. The operating temperatures (1150 and 850 °C) were set in the combustion tube and reduction tube, respectively. The ash content of the dried sludge was 45%, and was obtained by recording the weight of the remaining portion of the sample after it had been burned in a muffle furnace at 575 °C for 8 h.

Table 1
Major compound composition (% w/w) of the red mud analyzed using XRF.

Major oxides	CaO	SiO_2	Fe_2O_3	TiO_2	Al_2O_3	MgO	Na_2O	K_2O
Composition % w/w	44.69	27.99	11.60	5.36	7.34	2.01	0.58	0.43

2.2. Red mud

Fresh red mud was supplied by the Chongqing Company (Aluminum Corporation of China), in the form of damp-dry powder. The red mud sample was dried at 105 °C in an oven for 8 h and then ground with a mortar and pestle. Subsequently, it was sieved to pass through an 80 μm sieve and stored in a vacuum desiccator until used. The particle size distribution of the red mud, determined by using a Master Sizer 33370-45 (Malverns, UK), indicated that 78% of the particles are <48 μm. The surface area was 10.8 $m^2 g^{-1}$, as determined with a BET surface area analyzer (Quantachrome AUTOSORB-1, USA). The TC of the dried red mud was 824 mg/kg, with a TIC/TC of 98.86%, which was determined in the same way as with the sewage sludge. The major components in the red mud were determined using a SHIMADZU X-ray Fluorescence Spectrometer-1800, and the results are shown in Table 1.

2.3. Analytical methods

XRD patterns of the samples were determined by using a PHILIPS PAN analytical X'Pert X-ray diffractometer with a Cu Kα radiation source, in a 2θ range of 5–90° at a scanning rate of 2° min^{-1}. The micro-morphology of the samples was investigated using a Scanning Electron Microscope (SEM) and elemental composition was analyzed using an Energy Dispersive X-ray (EDX; JOEL model with an Ultimate resolution JSM-7800F, Japan). The pH measurements were made using a calibrated Orion 2 Star Bench top pH meter. The thermo-gravimetric analyses were done using a NETZSCH STA 449 F3 thermal analyzer (Germany), with air condition of 50 mL min^{-1}, heating speed of 15 °C min^{-1} and temperature range of 30–1000 °C. The levels of CO_2, SO_2 and nitrogen oxides (NO, NO_2) in the exhausts were measured using high-precision sensors.

2.4. Experimental set-up

The green SCWO set up included two, gas (air) sealing SCWO reaction vessels developed recently in our laboratory, which were stacked vertically and connected in series. The feedstock (suspension of sewage sludge and red mud), supercritical water, and oxidant (air) were pumped into the reaction vessels simultaneously from different inlets while the reaction proceeded. The feedstock was moved between reaction vessel (RV) 1 and RV2 with consideration of the time needed for heating up and its residence time. The supercritical water was pumped in from the bottom of RV1 mainly due to the roles it played both as an energy reservoir and as a strong upward flowing fluid. The air was utilized not only as an oxidant but also as a protective layer, so it was pumped from two inlets located in RV1 and another two located in RV2. In the reaction zone, in contrast to the upward flowing supercritical water, various solids (e.g., inorganic salts, red mud, sludge ashes) sank due to their greater density. The sinking solid particles were collected in a compact receptacle at the right bottom of RV1. Collisions between the sinking particles and the rising fluids favored better sludge oxidation, which is another attribute of the gas sealing SCWO reaction vessel. RV1 and RV2 have the same dimensions (e.g., 500 mm in height and with the effective diameter of 29.5 mm) and more information about the reactor performance