Chemical Engineering Science 144 (2016) 260–266

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Review

Alkyl aminated nanocelluloses in selective flotation of aluminium oxide and quartz

Ossi Laitinen [a,*], Robert Hartmann [a], Juho A. Sirviö [a], Henrikki Liimatainen [a], Martin Rudolph [b], Ari Ämmälä [a], Mirja Illikainen [a]

[a] University of Oulu, Fibre and Particle Engineering, P.O. Box 4300, FI-90014 Oulu, Finland
[b] Helmholtz Institute Freiberg for Resource Technology, Division of Processing, Halsbrücker Str. 34, 09599 Freiberg, Germany

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
7 January 2016
Accepted 25 January 2016
Available online 5 February 2016

Keywords:
Alumina
Collector
Flotation
Nanocellulose
Quartz
Selectivity

ABSTRACT

There are economic and ecological incentives for developing novel green chemicals from renewable resources in order to reduce the environmental impact of mineral processing. Cellulose, the most abundant natural polymeric source, is a promising green alternative that could replace the synthetic chemicals currently used. In this study, linear alkyl aminated nanocelluloses with increasing chain lengths were used for the selective flotation of aluminium oxide and quartz. Methylamine, ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine and *n*-hexylamine were introduced into a cellulose backbone using combined periodate oxidation and reductive amination in an aqueous environment. The hydrophobicity of the nanocelluloses was found to be increased by extending the alkyl chain length of the amino groups. Flotation experiments proved that alkyl aminated nanocelluloses can be both effective and selective collectors for quartz in a flotation system if they are sufficiently hydrophobic to allow the particles to effectively attach to the air bubbles. In the case of flotation with a known quartz and alumina mixture, the successful separation solution used aminated nanocelluloses at a pH of around 7.5.

Contents

* Corresponding author. Tel.: +358 503504960.
E-mail address: ossi.laitinen@oulu.fi (O. Laitinen).

http://dx.doi.org/10.1016/j.ces.2016.01.052
0009-2509/

1. Introduction

Aluminium is the third most abundant element in the Earth's crust and is one of the most commonly used metallic elements. The Bayer process is the most common commercial concentration process for the production of alumina from bauxite (Xu et al., 2004). In the Bayer process, bauxite is digested in a caustic soda solution at elevated temperatures under pressure, after which the solution contains the dissolved aluminium oxide in the form of sodium aluminate and the residue from the bauxite. This insoluble residue, called "red mud", consists predominantly of iron oxide, titania and silica, but also contains many trace metals, such as magnesium, chromium, cobalt, nickel, copper and zinc (Collins et al., 2014). The red mud is then separated from the aluminium oxide-rich solution, for instance with the aid of synthetic flocculants. The clarified liquor is further purified (mud particle removal) via filtration. Alumina trihydrate is then precipitated from the liquor, filtered and washed before the calcination is conducted at extremely high temperatures.

Ores with an Al_2O_3/SiO_2 mass ratio greater than 10 can be directly processed with the Bayer process (Massola et al., 2009). However, poorer ores must be processed beforehand in order to increase the Al_2O_3/SiO_2 ratio. For example, for a low-grade ore with an Al_2O_3/SiO_2 mass ratio below 8, a combination of sintering and the Bayer process has been used (Zhao et al., 2004). However, the very high energy consumption and negative environmental impacts associated with sintering processes reduce its feasibility and economic viability in the concentration process. Therefore, low-cost physical separation processes, for instance with selective grinding and flotation (Ou et al., 2007) or selective flotation (Liu et al., 2007; Wang et al., 2004; Xia et al., 2010; Xu et al., 2004), which enables direct application of the Bayer process, are highly desirable for increasing the Al_2O_3/SiO_2 mass ratio of ores.

Flotation is a physicochemical separation technique based on chemical differences in the surface wettability characteristics of the mineral species present in a pulp. The process utilises selectively-adsorbing chemical additives to modify the minerals' surface wettability properties, in order to maximise the selective separation of mineral species through the buoyance action of gas bubbles (Araujo et al., 2005; Huang et al., 2014). In most flotation systems, the particles of the valuable mineral are removed from the gangue (i.e. commercially worthless material that surrounds, or is closely mixed with, a wanted mineral in an ore deposit) via their attachment to gas bubbles and enrichment in the froth, which characterises direct flotation. In reverse or inverse flotation, gangue particles are removed by the froth while the concentrate remains in suspension (Filippov et al., 2010; Ma et al., 2011; Sahoo et al., 2015; Vieira and Peres, 2007). Reverse flotation can be useful for cases in which gangue comprised of silica or silicates is floated with an amine-type collector (i.e. surfactant chemical, which is imparted a hydrophobicity of minerals in order to float them in flotation overflow), while aluminium oxide particles are hydrated and enriched in the underflow fraction.

Future challenges in aluminium processing are related to the quality of the ores and the fact that the industry must be able to benefit from deposits of lower grades due to the increasing demand for sustainability, including the minimisation of water and energy consumption and of environmental emissions. Furthermore, there are economic and ecological incentives to develop novel green chemicals from renewable resources, in order to reduce the environmental impact of processing. For this purpose, cellulose, which is the most abundant natural polymeric source, represents a promising green alternative that could replace the present synthetic chemicals. In particular, cellulose nanoparticles, which have a very large specific surface area that can be covered with cationic, anionic and hydrophobic functional groups, are assumed to be beneficial for several water-treatment applications (Hokkanen et al., 2013; Liimatainen et al., 2012; Suopajärvi et al., 2013; Yu et al., 2013). For example, by attaching hydrophobic alkyl chains on the nanocellulose backbone (Laitinen et al., 2014; Visanko et al., 2014), bio-based collectors with selective performances could potentially be attained for several mineral oxides, as shown in our previous study (Hartmann et al., 2016).

In the present study, aminated nanocelluloses with various chain lengths were synthesised, and their ability to serve as quartz collectors in the mineral flotation process was addressed. Furthermore, the aim was to investigate the aminated nanocelluloses in a mixture of aluminium oxide and quartz, and to compare their flotation performances and selectivities with commercial quartz collectors (i.e. ether amine collectors).

2. Materials and methods

2.1. Materials

Aluminium oxide (purity ~99% Al_2O_3), also known as corundum powder, was obtained from Sigma-Aldrich (USA). Quartz (purity ~98% SiO_2) crystals were obtained from Sibelco Nordic Ltd. (Finland). Original quartz particles (median size approximately 400 μm) were ground in a laboratory ball mill (Retsch PM 200, Germany) for 5 min to obtain a suitable grain size fraction for flotation. The size distributions of aluminium oxide and quartz (after comminution), determined with a Beckman Coulter LS 320 particle size analyser, are presented in Fig. 1. The chemical compositions of minerals were characterised with an X-ray fluorescence spectrometer (XRF, PANalytical Axios^{mAX}). The content of the major components is shown in Table 1.

Alkyl ether monoamines (EDA and EDA-C) were provided by Clariant (Finland). Fresh solutions (1% ww^{-1}) of these reagents were prepared each day. Hydrochloric acid and sodium hydroxide were used to adjust each solution's pH to the desired level. Dowfroth 250C (Dow Chemical Company, USA) was used as a frother in all flotation tests to modify the surface tension of the water and to achieve a suitable bubble-size distribution for mineral flotation. Different aminocellulose modifications were synthesised in the laboratory, and their production is described step by step in the following chapter.

Chemicals for the periodate oxidation of cellulose ($NaIO_4$ and LiCl, USA) were obtained from Sigma-Aldrich. 2-picolineborane (Sigma-Aldrich, USA (95%)) and six primary, open chain amines were used for the reductive amination. These included: methylamine, *n*-propylamine, *n*-butylamine, and *n*-hexylamine hydrochloride; *n*-pentylamine

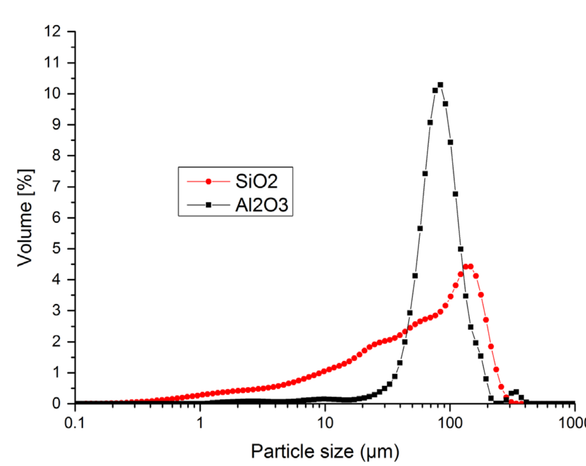

Fig. 1. Particle size distribution of aluminium oxide and quartz.