Combined oxidation and 2-octanol extraction of iron from a synthetic ilmenite hydrochloric acid leachate

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ABSTRACT

Separation of ferrous iron from titanium(IV) in a simulated ilmenite hydrochloric acid leachate by simultaneous oxidation and 2-octanol extraction was investigated. The effects of extraction time, organic/aqueous (O/A) phase ratio, temperature, and hydrochloric acid concentration were studied. Using pure oxygen as the oxidant and 100% (v/v) 2-octanol as extractant, the oxidation of ferrous iron and subsequent ferric iron extraction reached 99.3% and 86.1%, respectively. In addition, with an O/A ratio of 1:3, a hydrochloric acid concentration of 9.35 mol/L at 35 °C for 30 min, titanium co-extraction was not observed. Over two stages of cross-current operation, the total iron extraction reached 99.6%, again with no titanium co-extraction. Furthermore, ∼100% iron stripping was obtained through a single contact, using distilled water as the stripping liquor with an O/A ratio of 1:1. Thus, an almost complete separation of iron(II) from titanium(IV) in the simulated leachate was achieved. The composition of the extracted complex was determined to be $HFeCl_4 \cdot 5(2\text{-octanol})$. The kinetics of both the iron(III) extraction and stripping were rapid, while the iron(II) oxidation was slow despite a new reactor with significantly enhanced gas–liquid contact being employed. Further enhancement of the oxidation through catalysis is expected, and so an improved method of iron(II) extraction from titanium for use in a hydrochloric acid TiO_2 pigment production process is proposed.

1. Introduction

Titanium dioxide (TiO_2) is the most widely used white inorganic pigment, with applications in paint, paper, and plastic. Due to its unique physical and chemical properties, titanium dioxide is also used in sunscreen [1,2], cosmetics [3], and food additives [4]. In addition, TiO_2 is also a promising photo- and bio-activity catalyst, with potential for application in a range of fields [5,6].

The main commercial routes to TiO_2 production are the sulfate and the chloride processes. The sulfate process can use low-grade ilmenite directly as a raw material, however, the quality the pro-

duced TiO_2 is poor compared to that produced from the chloride process. In addition, for each ton of TiO_2 produced, the sulfate process produces approximately 8 tons of ∼20 wt.% spent sulfuric acid during the hydrolysis phase, and 100–250 tons of ⩽10 wt.% sulfuric acid or acid-containing wastewater during the washing section, which results in severe environmental problems [7–9]. The chloride process has a number of advantages over the sulfate process in terms of cost and waste management, and hence >60% of TiO_2 pigment plants worldwide are operated using the chloride process. However, this process requires a high grade of rutile ($TiO_2 \geqslant 90\%$ (w/w)) or high-titanium slag ($TiO_2 \geqslant 80\%$ (w/w)), along with toxic chlorine gas as raw materials [10,11].

Duyvesteyn et al. and Verhulst et al. [12,13] proposed a hydrochloric acid TiO_2 process (known as the Altair process), which can use low or medium grade ilmenite as a raw material. This process allows purification of the titanium and iron-containing leachate through solvent extraction, in which TRPO (a mixture of C_6 and C_8 trialkylphosphine oxides) was first employed to form pregnant strip liquor containing titanium and ferric ions and a ferrous-bearing raffinate. The strip liquor was then subjected to a second solvent extraction using Alamine 336 (tri-octylamine)

to extract the ferric ions. Since TRPO was unable to completely separate the titanium and ferric ions [14], a two-step extraction process was required, thus complicating the extraction process. Hence, further process optimization was required.

The extraction and separation of Ti(IV) and iron from hydrochloric acid solutions has been widely investigated. Three main kinds of extractants have been tested, including acidic organophosphorus extractants, such as di(2-ethylhexyl) phosphoric acid (DEHPA) [15–17], 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester (EHEHPA) [18,19], di-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) [20], di-2,4,4-trimethylpentyl dithiophosphinic acid (Cyanex 301), and di-2,4,4-trimethylpentyl monothiophosphinic acid (Cyanex 302) [21,22]. In addition, neutral solvent extractants have also been tested, including tri-*n*-butylphosphate (TBP) [23–29], TRPO [14,30–33], tri-*n*-octylphosphine oxide (TOPO) [21,22], and methyl isobutyl ketone (MIBK) [24,25,34–38]. Finally, amine extractants such as Alamine 336 (N235) [39,40], trioctylamine (TOA) [41], Aliquat 336 [42], and the chelating extractant 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) [43] have been tested.

Although the acidic organophosphorus extractants exhibited high Ti(IV) or Fe(III) extraction efficiencies, slow extraction kinetics (60–120 min), poor Ti/Fe selectivity, and problematic stripping prevented their widespread implementation. Among the neutral organophosphorus extractants, TBP, TOPO, and TRPO have been widely studied for separation of titanium from iron. Both TRPO and TOPO exhibit high extraction efficiencies. However, with >80% extraction of Fe(III), approximately 40% Ti(IV) was co-extracted, indicating poor selectivity [14,30,31]. In contrast, TBP exhibits a high selectivity of Fe(III) over Ti (IV). Using 6 M HCl, almost complete Fe(III) extraction was achieved with negligible titanium co-extraction [23–26]. However, when used for metal extraction from concentrated solutions, TBP posed two problems, namely the formation of a third phase, and poor phase separation (over 15–20 min) [24]. The neutral oxygen-containing extractant, methyl isobutyl ketone (MIBK), has also been widely studied in the extraction of Fe(III) from hydrochloric acid systems, in particular for the preparation of high purity iron compounds [24,25,34–37]. Yamamura et al. [36] investigated the extraction of Fe (III) from ilmenite hydrochloric acid leaching solution using 50% (*v/v*) MIBK in benzene or kerosene, achieving complete Fe(III) separation from other valuable metals through a three-stage extraction. However, this process required a hydrochloric acid concentration of >5.5 M.

Previous reports have shown that although a number of the above extractants have extremely high selectivity of Fe(III) over Ti(IV) in HCl, none can directly separate Fe(II) and Ti(IV). Thus, if iron is in its ferrous state, oxidation must be carried out prior to extraction. The oxidation of ferrous ion in HCl solution is generally carried out using toxic chlorine [25]. Chiba et al. [27] also investigated the use of air as an oxidant, as it is cheap and environmentally friendly. However, after 2 h, only ~31% oxidation of Fe(II) had been achieved. This is due to the gradually increasing redox potential of Fe^{3+}/Fe^{2+} in solution as oxidation progresses, thus resulting in a gradually decreasing driving force for oxidation. Thus, continuous removal of the formed Fe(III) would result in rapid progression of the oxidation reaction.

In our previous study [38], we report investigations into a simultaneous ferrous ion oxidation and MIBK extraction of ferric iron from a simulated ilmenite hydrochloric acid leachate. Iron extraction exceeded 97% in the absence of titanium co-extraction. However, a number of drawbacks were also evident, including the low flash point of MIBK (~15.6 °C), its high solubility in water (~2% (*v/v*)), and its volatility. More specifically, MIBK solubility in the simulated ilmenite hydrochloric acid leachate (9.35 mol/L HCl) was 0.0076 g/mL. Therefore, to reduce MIBK loss

in the extraction processes, an auxiliary process for the recovery of MIBK from the raffinate, strip liquor, and exhaust was required, thus complicating the process. It is therefore necessary to seek new a extraction system for this simultaneous oxidation and extraction process.

The neutral oxygen-containing extractant, 2-octanol, has been widely studied in the separation of niobium and tantalum [44–49], and Fe(III) and Co(II) [50]. Compared to MIBK, 2-octanol has a high flash point (~73 °C), lower water solubility (~0.08% (*v/v*)), and lower volatility. 2-Octanol solubility in the simulated ilmenite hydrochloric acid leachate with a hydrochloric acid concentration of 9.35 mol/L was significantly lower than that of MIBK, at 0.00075 g/mL. However, to date, the separation of titanium and iron from a simulated ilmenite hydrochloric acid leachate using 2-octanol as an extractant has not yet been reported.

We herein report investigations into the direct separation of titanium(IV) and iron(II) from a simulated ilmenite hydrochloric acid leachate using undiluted 2-octanol as the extractant and oxygen the as oxidant, through simultaneous oxidation and extraction. The effects of the oxidation and extraction conditions on the separation, the extraction complex composition, and the stripping of iron were investigated.

2. Materials and methods

2.1. Reagents and solutions

As for our previous study [51], we used a Panzhihua ilmenite hydrochloric acid leachate containing 61 g/L Ti(IV), 20 g/L Fe(II), and 6.8–9.4 M free HCl (after ferric–ferrous reduction with iron powder, partial crystallization, and removal of the $FeCl_2 \cdot 4H_2O$ crystals). Thus, the simulated ilmenite hydrochloric acid leachate (simulated leachate) was prepared according to the above titanium and ferrous iron concentration. A free hydrochloric acid concentration of 8.21 M was employed for all experiments, with the exception of those experiments where the effect of HCl concentration was studied. For comparison, a hydrochloric acid solution containing ferric chloride and titanyl chloride (ferric-containing HCl solution) was prepared according to the following chemical composition: 61 g/L Ti(IV), 20 g/L Fe(III), and 8.34 M free HCl. All the chemicals employed, including titanium tetrachloride, ferrous chloride, ferric chloride, and hydrochloric acid, were obtained from Chengdu Kelong Chemical Reagent Factory. All the reagents were of analytical reagent grade, and directly used without further purification.

2-Octanol (99%) was obtained from the Shanghai Laiyashi Chemical Reagent Factory. Oxygen and nitrogen (both 99.5%) were used in the experiments. All reagents were used as received without further purification.

2.2. Procedures

The simultaneous oxidation/extraction process was a gas–liquid–liquid multiphase reaction. As in our previous study, the overall rate of the simultaneous process was controlled by the oxidation step [38], which could be accelerated by decreasing the size of the oxygen bubbles. In our previous study, the size of the oxygen bubbles was controlled by bubbling through uniformly arranged holes (~1 mm diameter) on an annular tube. In the present study, oxygen was introduced to the bottom of a 1000 mL bubble reactor through a sand core gas distributor with average hole sizes of 3–4 μm, and then allowed to react with the chloride in solution. A mechanical stirrer was employed to mix two liquid phases. The reactor was heated using a water bath, with the temperature controlled to ±2 °C. In each test, 2-octanol (100 mL) and either the simulated leachate or ferric-containing HCl solution