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Utilization of a waste from titanium oxide industry for the synthesis of sodium ferrate by gas–solid reactions

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ABSTRACT

This work is focused on the preparation of alkali ferrates, especially sodium ferrate, using ferrous sulfate as iron bearing material and chlorine as oxidant. Ferrous sulfate heptahydrate is mainly generated during titanium oxide extraction from ilmenite through the sulfate route; it is considered as a waste for this industry. Obtained alkali ferrates belong to the compounds where iron is in the rare hexavalent state and they are becoming a substance of growing importance for water treatment and industrial effluent cleaning.

Two methods are developed for the ferrate synthesis. The first method consists of simultaneous reactions of two solids (iron sulfate and sodium hydroxide) and one gaseous oxidant (diluted chlorine). The second method involves a homogenous premixing of both solids prior to the oxidation by diluted chlorine. The synthesis process is performed in a rotary reactor at room temperature; however, since the overall reaction is exothermic, temperatures as high as 150 °C are often recorded. The effects of several parameters such as hydration extent of raw materials, Na/Fe ratio, chlorine content of the reactive gases on the sodium ferrate synthesis are investigated to determine the optimal processing conditions. The conversion efficiency of Fe(II) to Fe(VI) during the sodium ferrate synthesis reaches about 30%.

1. Introduction

As iron sulfate is chosen as raw material for the ferrate synthesis, it is appropriate to give a short description of the ferrous sulfate generation from TiO_2 industry. Titanium dioxide is produced from raw materials as ilmenite, rutile, anatase and slags using "sulfate" or "chloride" routes [1–3]. The sulfate process is usually involved for TiO_2 production from ilmenite and titanium slags. Eqs. (1) and (2) represent the main reactions occurring during the treatment of ilmenite by this process. Accordingly, ilmenite reacts with sulfuric acid generating a solution containing titanyl sulfate and iron sulfate.

$$FeTiO_3 + 5H_2O + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4{\cdot}7H_2O \tag{1}$$

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \tag{2}$$

The solution is treated with metallic iron to reduce ferric ions into ferrous ones, thus avoiding the precipitation of ferric hydroxide. Ferrous sulfate then crystallizes as $FeSO_4{\cdot}7H_2O$ and is separated from the liquor. Other steps are necessary to obtain TiO_2 from $TiOSO_4$. Another source of iron sulfate is the effluent of the surface treatment of steel. However, the amount of $FeSO_4{\cdot}7H_2O$ generated from this industry will decrease in the future due to the use of HCl instead of H_2SO_4.

The major environmental disadvantage of the sulfate process, for the TiO_2 production, is the large quantities of spent acid and ferrous sulfate generated. As could be expected, the amount of produced iron sulfate depends on the quality of the raw materials used for the TiO_2 production and it can reach up to 6 tons of $FeSO_4{\cdot}7H_2O$ generated per ton of produced TiO_2. In European countries, the production of TiO_2 is mainly covered through the sulfate route, which generates a huge amount of ferrous sulfate heptahydrate, while North American countries produce titanium oxide mainly through the chlorine technology. Only a few part of the iron sulfate is reused (*e.g.* in agriculture) and the rest has to be disposed as a waste. The discharge in the seawater of waste coming from TiO_2 industry is no longer allowed as noted in the directive 92/112/EEC [3].

In this context, the present work aims at using industrial iron sulfate for synthesizing alkali ferrates, mainly sodium ones.

The denomination "ferrate" is usually attributed to compounds containing iron in an oxidation state higher than Fe^{III}. Though the ferrates (IV, V and VI) are cited in the literature, the ferrate(VI) $[FeO_4^{2-}]$ seems to be the best known and the most studied of them.

The importance of the synthesis of ferrates is related to their considerable and innovating applications in different fields. The reduction of ferrate ion (FeO_4^{2-}) in aqueous solution generates

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both ferric hydroxide precipitate and nascent oxygen, as shown by Eq. (3). Ferrate is used for water treatment due to its powerful oxidizing capacity (oxidation of organics and mineral materials, biocide agent) and to the flocculating property of the resulting ferric hydroxide [4]. The ferrates can replace chlorine in the pre-oxidation stage of water and partly the iron or aluminum salts [$FeCl_3$, $AlCl_3$ and $Al_2(SO_4)_3$] commonly used for coagulation and flocculation. Furthermore, the decomposition of the ferrate according to Eq. (3) generates a basic media favoring the precipitation of heavy metals as hydroxides. These properties exhibited together by one single compound make the ferrate an ongoing material particularly interesting and valuable for water treatment. Recently, potassium ferrate alone and coupled with $FeCl_3$ and $AlCl_3$ is used for removal of arsenite and arsenate from drinking water [5]. Yngard et al. [6] achieved the complete removal of cyanide present in zinc plating rinse water by using Fe(VI).

$$2FeO_4{}^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 4OH^- + 3O^{\bullet} \tag{3}$$

The most attractive property of the ferrate ion is its strong oxidizing ability. The redox potentials of the Fe(VI)/Fe(III) couples [$E^\circ(FeO_4{}^{2-}/Fe^{3+})$ and $E^\circ(FeO_4{}^{2-}/Fe(OH)_3)$] are 2.20 and 0.72 V, respectively at pH 1 and 14. These values are significantly higher than those corresponding to the Mn(VII)/Mn(IV) [$E^\circ(MnO_4{}^-/MnO_2) = 1.679$ and 0.588 V at pH 1 and 14, respectively] or Cr(VI)/Cr(III) couples [$E^\circ(Cr_2O_7{}^{2-}/Cr^{3+}) = 1.33$ V in acidic medium, $E^\circ(CrO_4{}^{2-}/Cr(OH)_3) = -0.12$ V in basic medium]. Using ferrate as an oxidant instead of chromate and/or permanganate is a promising choice from the environmental point of view. The ferrate reduction products are harmless for humans and the environment since they are mainly composed of iron oxy/hydroxides.

Many recent investigations are devoted to ferrates. A book describing a comprehensive overview on the chemistry, properties, synthesis and uses of ferrates to treat contaminants in water, wastewater, and industrial effluents is already available [7]. The possible formations of iron in unusual oxidation states, +7 and +8 are also discussed there. A review of the research progress concerning the use of ferrate(VI) for environmental remediation is given by Jiang [8]. The kinetics and mechanisms related to the oxidation of inorganic compounds by ferrates are recently reviewed by Sharma [9]. Other studies are devoted to the development of alkaline super-iron batteries based on potassium ferrate [10,11].

Most of works and investigations devoted to synthesis and applications of ferrates are performed at laboratory scale, which results from difficulties related to the preparation methods, to the ferrates low stability and to their preparation cost. Well known methods consist of chemical and/or electrochemical oxidation of iron salts in alkali solutions. Recent developments on the electrochemical synthesis of ferrates are well described by Mácová et al. [12]. However, the Fe^{VI} efficiency of wet synthesis methods should be low due to its reaction with water (Eq. (3)) suggesting the use of strong alkali solutions to improve the ferrate yield. As mentioned early [13], one possibility to enhance the ferrate stability and decrease the cost of potassium ferrate [K_2FeO_4] synthesis was to use iron sulfate as a raw material and develop a dry route for its synthesis.

The aim of the present work is to extend the dry method for synthesizing sodium ferrate by gas–solid reactions using chlorine as oxidant. It must be mentioned that using NaOH instead of KOH for ferrate synthesis would decrease the synthesis cost. Further, end-uses of sodium ferrate, especially for water treatment, will be more advantageous since the allowed limit for sodium content in water is more flexible than that of potassium. To our knowledge, no prior published work deals with the dry synthesis of sodium ferrate at room temperature *via* gas–solid reactions. Effects of several parameters on the kinetic of ferrate synthesis and on the Fe(VI) efficiency are also investigated in this work.

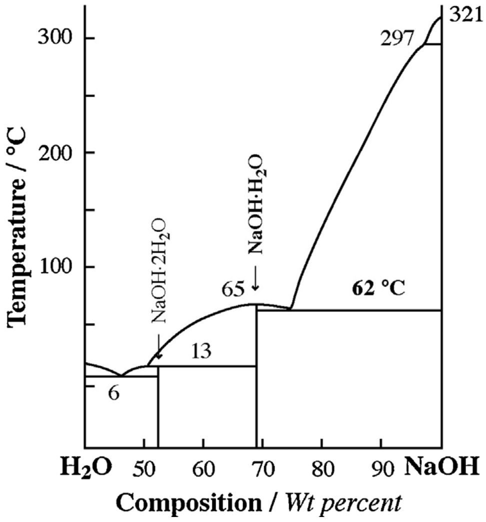

Fig. 1. Phase diagram of water–sodium hydroxide system [17].

Recently a new process for the preparation of sodium ferrate is proposed [14] in order to overcome some difficulties observed during its synthesis in rotary reactor. This process includes a step of premixing of NaOH with iron sulfate at solid state followed by the sodium ferrate synthesis of the obtained mixture in a fluidized bed. A better control of temperature and water content in the reaction zone improves significantly the Fe(VI) efficiency of the sodium ferrate synthesis.

2. Materials and experimental procedures

Six samples ($S_1, \ldots, S_6$) of ferrous sulfate issued from titanium dioxide and surface treatment of steel industries are collected. Another sample of analytical grade (S_0), designed as reference sample, is also used to compare its behavior with those of industrial ones. Scanning electron microscope (SEM), X-ray diffraction (XRD), and chemical analyses are used to determine the composition of these ferrous sulfate samples. The oxidation state of iron (Fe^{II} and Fe^{III}) of the samples is determined by Mössbauer spectroscopy (MS) technique described early [15]. The chemical composition of these samples ($S_0, S_1, \ldots, S_6$) is presented in Table 1. These samples contain about 20% iron and 35% sulfate (theoretical composition of $FeSO_4{\cdot}7H_2O$ is 20.09% iron and 34.55% sulfate). This confirms that the industrial sulfate samples are almost pure. The quasi totality of iron is found to be in divalent state (except S_4 that contains about 2% Fe^{III}) and the major phase in all samples is $FeSO_4{\cdot}7H_2O$. The heavy metal (Zn, Cu, Pb, Cr, Cd, . . .) content is low, confirming indirectly that $FeSO_4{\cdot}7H_2O$ is separated from the liquor by crystallization. The high purity of ferrous sulfate samples from TiO_2 industry is also mentioned by Gázquez et al. [16].

The sodium hydroxide (NaOH) used for the ferrate synthesis is anhydrous. The mean diameter of the NaOH particles (beads) is about 1 mm. Note that the potassium hydroxide pellets used early [13] for the ferrate synthesis had a diameter of about 5 mm and that potassium hydroxide contained about 15% H_2O (by weight). The gaseous reagents (Cl_2, N_2, O_2) used here have a purity higher than 99%.

A particular attention is devoted to the preparation of $NaOH + xH_2O$ and $NaOH + KOH + xH_2O$ mixtures prior to the ferrate synthesis. Data from the phase diagram of the H_2O–NaOH system [17] (Fig. 1) are used for preparing NaOH containing variable amount of H_2O. Here, the relevant part of this diagram is the one corresponding to water contents < 31% (by weight) within the $NaOH{\cdot}H_2O$–NaOH system. As an example, the preparation of