Surface Chemical Characterization of Bastnaesite through Electrokinetics†

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Abstract

The surface properties of the synthesized Ce-bastnaesite were determined by the electrophoresis technique. The point of zero charge (PZC) of this mineral occurs at pH 7.8. A sample of natural bastnaesite [(Ce, La) FCO3] from the Mountain Pass deposit in California, USA was also studied through electrokinetic measurements. The mineral was found to behave essentially like a carbonate with its PZC occurring at pH 9.2 and pCO3 6 in aqueous solutions. The isoelectric point of synthetic Ce-bastnaesite as obtained by equilibrium pH measurements occurs around pH 7.8, which agrees reasonably well with the equionic point of pH 7.3, computed on the basis of thermodynamic data and pH of minimum solubility for Ce bastnaesite, namely pH 7.6. Measurements reported in the literature on relatively pure samples of bastnaesite do exhibit PZCs closer to the value of pH 7.8, as measured by us for synthetic Ce-bastnaesite.

Keywords: bastnaesite, electrokinetics, adsorption, lignin sulfonate, synthesis of Ce bastnaesite, Mountain Pass rare-earth deposit, electrophoretic mobility, zeta potential

1. Introduction

Bastnaesite [(Ce, La) FCO3], a rare-earth fluorocarbonate, is an important commercial mineral constituent of major rare-earth ore deposits in the world, such as at Mountain Pass in California, USA and Baiyan Obo in Inner Mongolia, China. Rare-earths have become critical to society because of their advanced technology applications such as smart phones, medical devices and jet engines (Tien, 2013). China holds about 50 % of the world’s total reserves of rare-earths and until recently was responsible for nearly 95 % of global supplies. Due to recent cutbacks in the Chinese exports of rare-earths, there is a renewed interest in the discovery, development and exploitation of rich rare-earth ore deposits in the world (Jordens et al., 2013; Zhang and Edwards, 2013; Gleason, 2011).

Bastnaesite is selectively floated using fatty acids and alkyl hydroxamates as collectors and sodium carbonate and ammonium lignin sulfonate as depressants from such associated gangue minerals as calcite and barite (Pradip, 1981; Fuerstenau et al., 1982; Pradip and Fuerstenau, 1991; Pradip and Fuerstenau, 2013). Bastnaesite belongs to and occurs in nature along with the family of sparingly soluble minerals such as fluorite, calcite, barite, fluorapatite and dolomite. The selectivity of flotation separation of bastnaesite in such systems is controlled by the surface chemistry of sparingly soluble minerals and the aqueous solution chemistry consisting of soluble ions contributed by the minerals and the added reagents. The surface chemistry of sparingly soluble minerals, including rare-earth minerals like bastnaesite, has been reviewed recently (Zhang et al., 2013). We present in this paper our results on the surface-chemical characterization of bastnaesite with the help of electrophoretic mobility measurements both on a natural mineral sample from Mountain Pass, California and also on a synthetic Ce-bastnaesite synthesized by us in our laboratory.

2. Materials and methods

A relatively rich sample of natural bastnaesite was selected for the electrokinetic experiments. It was possible to handpick pure bastnaesite particles from a crushed ore sample with a UV lamp since bastnaesite fluoresces with a distinctive green color under unfiltered UV light. The hand-picked sample was then washed and ground to minus 37 μm in an agate vibratory mill. The chemical analysis of the powder assayed 57.4 % REO (as compared
The impurities in the sample were analyzed to be 8.8 % BaO, 1.6 % CaO and 0.4 % SrO.

The synthetic Ce bastnaesite used in this study was prepared in the laboratory as per the method described in our earlier publication (Pradip, 1981; Li, 1982; Pradip et al., 2013).

A suspension containing 0.05 % of the finely ground mineral was ultrasonically dispersed and conditioned overnight (unless otherwise specified) for equilibration before making the electrokinetic measurements. The electrophoretic mobility of bastnaesite particles was measured using a Riddick Zeta Meter (Model 3.0). The pH was controlled by an appropriate addition of HNO₃ and NaOH. Unless stated otherwise, we have reported our results after 24 hours of equilibration.

For investigation of solubility/pH effects, air saturated, triple distilled water was adjusted to various initial pH values using HNO₃ and NaOH. Then 0.5 g of synthetic Ce-bastnaesite was added to 250 ml of these solutions contained in polyethylene bottles and conditioned in a Environ-Shaker at 25 °C for one minute. The pH measured at this point was recorded as initial pH. Mixing was continued for 28 hours for equilibration. The solids were centrifuged out and the total concentration of carbonate, fluoride and cerium in the supernatant were determined as described previously (Pradip et al., 2013).

3. Results and Discussion

3.1 Estimation of the PZC of synthetic bastnaesite by pH measurements

Starting at eight different initial pH’s, the change in solution pH in presence of synthetic bastnaesite as a function of conditioning time was measured. The results are summarized in Fig. 1. For initial solution pH’s above 7, the pH was observed to decrease with conditioning time whereas for starting pH’s below 7, the pH increased towards 7. The results thus suggest that the PZC of synthetic Ce bastnaesite lies close to pH 7. It is interesting to note that this pH is also close to the pH range of minimum solubility for Ce-bastnaesite, as illustrated in our earlier paper (Pradip et al., 2013).

3.2 Electrokinetic measurements on synthetic bastnaesite

The electrophoretic mobility of synthetic Ce-bastnaesite was measured as a function of pH and conditioning time. For all sparingly soluble minerals, it requires some conditioning time before the surface reaches an equilibrium with the solution phase.

In order to delineate the potential determining ions for bastnaesite, the electrophoretic mobilities were measured in the presence of NaF and Na₂CO₃ in solution. The results presented in Fig. 2 for one minute conditioning indicate that the addition of NaF has negligible influence on the electrophoretic mobility as compared to Na₂CO₃ in solution (Fig. 3), particularly at alkaline pH. NaF does seem to adsorb specifically at acidic pH. With the addition of 1 mM Na₂CO₃ in solution, the IEP (isoelectric point) of bastnaesite shifts by one pH unit (Fig. 3). It is interesting to note that the electrophoretic mobility-vs-pH curves for synthetic Ce-bastnaesite for NaNO₃ and Na₂CO₃ in solution are identical and the IEP is at pH 7.8 after 24 hours of conditioning (Fig. 4).

It is indeed noteworthy that the experimentally determined values for the PZC of synthetic Ce-bastnaesite, namely pH 7.8, agrees well with the equal ionic point of pH 7.3 (Fig. 5) of the solution phase in equilibrium with bastnaesite. This point was computed using the thermodynamic data provided in our earlier publication (Pradip et al., 2013). In terms of pH, the equal ionic point of the solution can be regarded as the PZC of the corresponding solid, provided that all ionic species have equal affinity for the surface. Assuming that the free ions and the hydroxy complexes adsorb at the surface with similar affinity, it is possible to compute the PZC from such thermodynamic calculations. Chander and Fuerstenau (1979,
1982) predicted the PZC for fluorapatite by this method. Their predicted values for fluorapatite agreed well with experimental results. Similar calculations for oxides and complex silicates reported by Parks (1965, 1967) also indicated good agreement with experimentally determined PZC values.

3.3 Electrokinetic measurements on natural bastnaesite

Electrophoretic mobility results obtained with a natural bastnaesite (57.4 % REO) sample from Mountain Pass are summarized in Fig. 6. The isoelectric point for natural bastnaesite was observed to occur at pH 9.2 as compared to pH 7.8 for synthetic Ce bastnaesite. In this case also, fluoride ion seems to strongly adsorb at the bastnaesite interface in the acidic pH range. The electrokinetic behavior in the presence of NaF suggests a surface reaction is occurring at the interface. Detailed computations on the solution equilibria of Ce bastnaesite as reported by Herrera-Urbina et al. (2013) clearly indicate that the bastnaesite surface is converted into cerium fluoride (CeF₃) in the acidic pH range, in particular below pH 6. Our observations suggesting strong adsorption and surface reaction leading to eventual conversion of the bastnaesite surface into cerium fluoride both with natural bastnaesite as well as synthetic Ce bastnaesite in the presence of NaF, is consistent with the conclusions drawn by Herrera-Urbina et al. (2013) on the basis of theoretical computations.

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The addition of 1 mM of Na₂CO₃ on the other hand results in a shift of one pH unit in the IEP of natural bastnaesite (Fig. 6). At lower carbonate concentrations, the effect is not significant. It is of course well understood that for sparingly soluble minerals, the interpretation of electrokinetic data is a little more involved since a sub-

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**Fig. 2** Electrophoretic mobility of synthetic cerium bastnaesite as a function of pH in the presence and absence of NaF.

**Fig. 3** Electrophoretic mobility of synthetic cerium bastnaesite as a function of pH in the presence and absence of sodium carbonate (1 minute conditioning).

**Fig. 4** Electrophoretic mobility of synthetic cerium bastnaesite as a function of pH in the presence and absence of sodium carbonate (24 hour conditioning).

**Fig. 5** Change of net charge with pH in the synthetic cerium bastnaesite/water system in equilibrium with the atmosphere at 25°C (room temp.)
stantial fraction of the potential determining ions are contributed to the solution phase as a consequence of mineral dissolution. For example, the contribution of Ce\(^{3+}\), F\(^{-}\) and CO\(_3^{2-}\) due to dissolution of bastnaesite can be as high as 10\(^{-3}\) M to 10\(^{-1}\) M. This is perhaps the reason why no significant influence of addition of electrolytes containing potential determining ions has been observed for concentrations less than 10\(^{-3}\) M. Moreover, it is difficult to perform electrophoretic mobility measurements at higher ionic strength. It is therefore preferable to conduct surface titration studies on such systems for determining the PZC (Fuerstenau, 1970; Fuerstenau and Pradip, 2005).

Since F\(^{-}\) and CO\(_3^{2-}\) ions are the lattice constituents of bastnaesite, the electrophoretic mobilities were measured as a function of the concentration of their corresponding soluble salts (NaF and Na\(_2\)CO\(_3\)). As illustrated in Fig. 7, the results suggest that carbonate ions are potential determining ions for bastnaesite. The effect of fluoride ions is not significant at around pH 9, the natural pH for natural bastnaesite. As we had discussed earlier, the bastnaesite surface responds to fluoride ions in the acidic pH range. In fact below pH 6 the surface is converted into CeF\(_3\).

It is also important to note that as compared to the PZC of synthetic bastnaesite (pH 7.2), the PZC of natural bastnaesite is found to occur at pH 9.2. The discrepancy between the two might result from two main factors, namely (i) the presence of calcite and barite in the natural bastnaesite sample used in this work and (ii) differences arising from the presence of other rare-earths in the natural bastnaesite as compared to synthetic Ce-bastnaesite. More detailed investigations are needed to delineate these effects.

Sodium carbonate and lignin sulfonate are used as depressants in the flotation separation of bastnaesite from associated gangue minerals (barite and calcite). We have measured the electrophoretic mobility of bastnaesite in the presence of an increasing concentration of ammonium lignin sulfonate at pH 9, and the results are presented in Fig. 7.

The electrophoretic mobilities of bastnaesite in the presence of lignin sulfonate are comparable to those measured with sodium carbonate. While the addition of sodium carbonate results in charge reversal since carbonate is a potential determining ion for bastnaesite, the charge reversal caused by lignin sulfonate is due to something else, namely that it adsorbs specifically at the bastnaesite/water interface. It is interesting to note that lignin sulfonate does have strong affinity for the bastnaesite surface. Earlier we published our work on the role of lignin sulfonate in the selective flotation of bastnaesite from associated gangue minerals in Mountain Pass Ore (Pradip, 1981, Pradip and Fuerstenau, 1991).

There are only a few publications that report the results of measurements of the electrokinetic behavior of bastnaesite. Houot et al. (1991) and Zhang et al. (2013) have attempted a comparison of published pH values for the PZC’s of bastnaesite from different sources. We present an updated version of their compilation in Table 1.

In addition to the source, we have also included the corresponding purity, wherever available, of the bastnaesite samples used for electrokinetic studies along with the PZC values reported by various researchers. The
results show an interesting trend. It is remarkable to note from the results summarized in Table 1 that relatively pure bastnaesite samples do exhibit a PZC closer to pH 7.8, the PZC reported for the pure synthetic Ce-bastnaesite, prepared in our laboratory.

### 3.4 Mechanism of surface charge generation

Bastnaesite belongs to the family of sparingly soluble salt-type minerals, such as fluorite, calcite, barite, apatite and scheelite. A distinctive feature of these minerals is that both the solvent constituent ions (H\(^+\) and OH\(^-\)) and the lattice ions, as well as their complexes with the solvent species, are found to be potential determining. For example, for calcite, aqueous species of the kind, \(3HCO_3^-\), \(3CO_3^{2-}\), \(Ca^{++}\), \(3CaHCO_3^+\), and \(CaOH^+\) have all been shown to determine the potential at the mineral/water interface (Somasundaran and Agar, 1967). These ionic species may be produced at the solid/solution interface or may form in bulk solution and subsequently adsorb at the interface. In the case of calcite, based on the available thermodynamic data, the point of zero charge, PZC, was calculated to occur at pH 8.2 assuming that the equal ionic point of the solution corresponds to the PZC of the mineral. This approach was first suggested by Parks and deBruyn (1962), who also pointed out that the equal ionic point would also correspond to the point of minimum overall solubility of the solid at which the total concentration of negative potential determining ions is equal to the total concentration of positive potential determining ions in the bulk and at the interface.

All soluble minerals exhibit a point of zero charge with respect to pH and hence H\(^+\) and OH\(^-\) ions are considered as the potential determining ions for sparingly soluble minerals also.

Foxall et al. (1979) had however questioned the assumption that H\(^+\) and OH\(^-\) ions can be regarded as potential determining ions for the salt type minerals in the same way as Ag\(^+\) and I\(^-\) are for AgI. According to these authors, the lattice constituent ions alone can be considered to be “potential determining” since the Nernstian relationship of the kind

\[
\psi_0 = -\frac{2.303RT}{zF}(pM - pM_{PZC}) \tag{1}
\]

is valid for these lattice ions only. Here \(\psi_0\) is the surface potential, \(R\) the gas constant, \(T\) the temperature, \(z\) the valence of the ion and \(F\), the Faraday constant. A change of pH can have the important but secondary effect of producing species of the kind described above, altering the balance of the ions present and thus the particle charge. In so far as pH determines the concentration of Ca\(^{++}\) concen-
ternary solution in equilibrium with calcite, it may have substantial influence on the surface potential of calcite.

The mechanism of surface charge generation for minerals that are tri-ionic crystals, such as bastnaesite (or fluorapatite) is even more complex. As pointed out by Saleeb and deBruyn (1972) for apatites, the concentration of any two ions can be varied independently for such solids and one can still maintain a constant solubility product. The ionic equilibrium for Ce-bastnaesite in aqueous solution, for example, can be represented as

$$\text{CeFCO}_3 = \text{Ce}^{+++} + \text{F}^{-} + \text{CO}_3^{--}$$  \hspace{1cm} (2)

for which

$$K_{sp} = \left[\text{Ce}^{+++}\right][\text{F}^{-}][\text{CO}_3^{--}]$$  \hspace{1cm} (3)

where the brackets denote the activities of corresponding ions in aqueous solution. If the concentration of these three potential determining ions, namely Ce-$$^{+++}$$, F- and CO$$^{--}$$ are plotted on three mutually perpendicular axes, a “solubility surface” may be constructed. The coordinates of all points lying on this surface will satisfy the conditions for heterogeneous equilibrium given by Eqn. 2. On this surface one may then locate a line or curve connecting, in principle, an infinite number of PZCs. Chander and Fuerstenau (1979) had analysed the PZC of hydroxyapatite along these lines. In contrast, for a di-ionic solid like AgI, this surface is only a line and therefore only one PZC is observed, if specific effects are excluded (Parks, 1965).

Furthermore, since the concentration of CO$$^{--}$$ ions is strongly dependent on pH, H$$^{+}$$ and OH$$^{-}$$ ions indirectly determine the potential of the bastnaesite/water interface. The solution equilibria can be represented as follows

$$\text{CO}_3^{--} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^{-} + \text{OH}^{-}$$  \hspace{1cm} (4)

$$\text{HCO}_3^{-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^{-}$$  \hspace{1cm} (5)

where

$$\varphi_0 = \frac{RT}{3F} \ln \left( \frac{[\text{Ce}^{+++}]}{[\text{Ce}^{+++}]_{PZC}} \right) = \frac{-RT}{F} \ln \left( \frac{[\text{F}^{-}]}{[\text{F}^{-}]_{PZC}} \right)$$

$$= \frac{-RT}{2F} \ln \left( \frac{[\text{CO}_3^{--}]}{[\text{CO}_3^{--}]_{PZC}} \right)$$  \hspace{1cm} (6)

Thus the double layer surface potential $$\varphi_0$$ for bastnaesite/water interface may be defined by the Eqn. 6, where the brackets denote the corresponding activities of the ions in solution.

Our electrokinetic studies show that in NaNO$$^3$$ solutions, the isoelectric point of natural bastnaesite occurs at pH 9.25. In the presence of Na$$^2$$CO$$^3$$ solutions, charge reversal takes place at $$3.7 \times 10^{-5} \text{ M Na}_2\text{CO}_3$$ with ionic strength and pH variable in these experiments. Knowing the pH and the total carbonate concentration CT, the concentration of carbonate ions can be calculated by the following Eqn. (Pradip, 1981; Fuerstenau et al., 1992)

$$[\text{CO}_3^{--}] = \left[ \frac{C_T}{[1+10^{10.3}[\text{H}^{+}]+10^{16.7}[\text{H}^{+}]^2]} \right]$$  \hspace{1cm} (7)

where [CO$$^{--}$$] is the concentration of carbonate ions in the bulk under these conditions. Table 2 summarizes these calculations.

A plot of zeta potential-vs-pCO$$^3$$ exhibits a straight line with a slope of $$-9.4 \text{ mV}$$ as compared to the theoretical Nernstian slope of $$-29.5 \text{ mV}$$ for carbonate ions. The zeta potential reversal takes place at pCO$$^3$$ = 6 that is, [CO$$^{--}$$] = $$10^{-6} \text{ M}$$.

4. Summary

The surface properties of synthetic cerium bastnaesite as well as a sample of natural bastnaesite sample from Mountain Pass, USA were studied by the electrophoresis technique. The PZC of synthetic bastnaesite was measured to occur at pH 7.8 as compared to pH 9.25 and pCO$$^3$$ 6 for natural bastnaesite. The differences in the PZC can be attributed to the impurities present in the natural sample. A comparison with PZC values for bastnaesite reported in the literature indicates that relatively pure samples of bastnaesite do exhibit PZC closer to pH 7.8, as measured by us for pure synthetic bastnaesite. The PZC of synthetic bastnaesite was found to be pH 7, as determined through equilibrium pH experiments. This value correlates well with those predicted on the basis of thermodynamic calculations. The equal ionic point for the solution phase in equilibrium with the bastnaesite surface

<table>
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<tr>
<th>Total sodium carbonate added</th>
<th>Equilibrium pH of the bastnaesite suspension</th>
<th>[CO$$^{--}$$]</th>
<th>pCO$$^3$$</th>
<th>Electrophoretic Mobility in μm/s per V/cm</th>
<th>Zeta Potential (mV)</th>
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<tr>
<td>$$10^{-5}$$</td>
<td>7.7</td>
<td>$$2.4 \times 10^{-8}$$</td>
<td>7.6</td>
<td>+1.16</td>
<td>+14.9</td>
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<tr>
<td>$$10^{-4}$$</td>
<td>9.3</td>
<td>$$9.1 \times 10^{-6}$$</td>
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<td>-0.73</td>
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<tr>
<td>$$10^{-3}$$</td>
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<td>$$5 \times 10^{-4}$$</td>
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<td>-1.98</td>
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<td>$$10^{-2}$$</td>
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<td>$$8.3 \times 10^{-3}$$</td>
<td>2.1</td>
<td>-2.2</td>
<td>-28.2</td>
</tr>
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</table>
Acknowledgements

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**Author’s short biography**

**Pradip**

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**Charles C. H. Li**

After graduating from Central South Institute of Mining and Metallurgy in Changsha, Charles Li entered the University of California at Berkeley to pursue graduate studies in mineral processing, and obtained his M.S. degree in 1982 and Ph.D. degree in 1986. He then joined CRA (now Rio Tinto) in Australia where he worked as a research engineer on mineral processing problems until his retirement.

**Douglas W. Fuerstenau**

After receiving his Sc.D. degree at MIT, Dr. Fuerstenau spent a six year period teaching at MIT and working in industry, after which time he joined the faculty of the University of California. At Berkeley he established an extensive program of teaching and research in minerals processing, applied surface chemistry and particle technology. With his graduate students and postdoctoral researchers, he has published a wide range of seminal papers in this field. He currently is P. Malozemoff Professor Emeritus of Mineral Engineering in the University of California.