

REACTIONS OF IRON MINERALS IN SODIUM ALUMINATE SOLUTIONS

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Settling properties of bauxite residue are affected by the form of iron mineral present in the system. The two forms of iron minerals generally found in bauxites are aluminous goethite, α -(Fe,Al)OOH and hematite, α -Fe₂O₃. Model systems comprising of synthetic goethite and hematite in pure sodium aluminate solutions were used to study reactions representative of those occurring in the Bayer Process. Hematite exhibits considerably faster settling rates as compared to those of goethite, owing to the surface properties unique to each mineral. Transformation of α -FeOOH \rightarrow α -Fe₂O₃ at high temperatures leads to improved settling. The kinetics and mechanism of this transformation reaction have been established. The transformation proceeds via a dissolution, reprecipitation mechanism. Factors that affect each step in the mechanism influence the overall reaction and, hence, clarification. These factors include: temperature, liquor composition, and presence of hematite seed. Also reported is the effect of temperature and liquor composition on the dissolution of goethite.

Introduction

Clarification is a critical step in bauxite processing and can limit the capacity of a Bayer plant. It is affected by variations in both the processing conditions and the quality of the bauxite. Clarification problems have often been associated with bauxites rich in goethite (α -FeOOH). The adverse effect of goethite on the settling behavior of red muds has been attributed to its fine particle size and unique surface properties. Furthermore, goethitic bauxites tend to have a lower alumina extraction yield because Al cations, that are often isomorphically substituted in the goethite lattice, cannot readily be extracted.

Extraction yield and sedimentation properties are known to improve considerably during high temperature digestion (1,2,3). It is believed this effect may be attributed in part to the conversion of goethite crystals to hematite (α -Fe₂O₃), the other form of iron mineral found in bauxites (2,3). This report covers an investigation of the goethite-to-hematite transformation, the variables that affect it and the significance of this conversion with regard to settling properties of the iron minerals.

Experimental

To avoid any interference from other minerals found in the bauxite residue, simple model systems comprised of well characterized iron oxides were used. Physical data for all samples are given in Table I. Surface area was determined by nitrogen adsorption, using a Micromeritics BET Surface Area Analyzer. Composition of the caustic liquors used is given in Table II. Pure sodium aluminate solutions were used to exclude any effects of contaminants usually found in the Bayer liquor. Transformation and solubility tests were also carried out in pure NaOH solutions with concentrations (expressed as Na₂O) varying from 25-200 g/L.

Table I. Physical Data for Iron Oxides*

| Iron Oxide No. | General Formula | Particle Shape | Particle Size (μ) | Specific Gravity | Surface Area (m ² /g) |
|----------------|--|----------------|-------------------------|------------------|----------------------------------|
| R03097 | α -Fe ₂ O ₃ | Rhombohedral | 0.25 | 4.90 | 12.5 |
| R2200 | α -Fe ₂ O ₃ | Spheroidal | 0.25 | 5.15 | 11.7 |
| R5098 | α -Fe ₂ O ₃ | Spheroidal | 0.50 | 5.15 | 7.6 |
| R8098 | α -Fe ₂ O ₃ | Spheroidal | 0.90 | 5.15 | 4.1 |
| Y02087 | α -FeOOH | Acicular | 0.50 | 4.03 | 16.8 |
| Y03587 | α -FeOOH | Acicular | 0.70 | 4.03 | 14.8 |
| Y08087 | α -FeOOH | Acicular | 1.50 | 4.03 | 7.7 |

* Pfizer Pigments color oxide technical data

Table II. Composition of Synthetic Liquors

| Solution No. | NaOH as Na ₂ O (g/L) | Moles Na ₂ O | Al ₂ O ₃ (g/L) | Moles Al ₂ O ₃ | Molar Ratio Na ₂ O/Al ₂ O ₃ |
|--------------|---------------------------------|-------------------------|--------------------------------------|--------------------------------------|--|
| 1 | 150 | 2.42 | 62 | 0.605 | 4.0 |
| 2 | 200 | 3.23 | 82 | 0.805 | 4.0 |
| 3 | 250 | 4.03 | 103 | 1.00 | 4.0 |
| 4 | 150 | 2.42 | 165 | 1.61 | 1.5 |
| 5 | 200 | 3.23 | 220 | 2.15 | 1.5 |
| 6 | 250 | 4.03 | 274 | 2.69 | 1.5 |
| 7 | 150 | 2.42 | 99 | 0.968 | 2.5 |
| 8 | 200 | 3.23 | 132 | 1.292 | 2.5 |

All transformation work was carried out in continuously stirred Monel autoclaves. Experimental temperature varied between 150-250°C and the maximum duration of tests was 48 hours. Both pure goethite (Series A) and a 1:1 mix of hematite + goethite (Series B) were used as starting material. Average particle size of the goethite and hematite (Pfizer Pigments) used was 0.5 μm. The concentration of solids was maintained at 50 g/L. X-ray diffraction (XRD) with Co-Kα radiation was used to determine the goethite and hematite content of samples. The iron oxide powders were also analyzed by transmission electron microscopy (TEM).

Solubility tests were conducted using caustic solutions and natural, coarse goethite. Natural goethite was used in the form of large pieces to avoid the ejection of any fines from the autoclave during sampling of the solution. The time of equilibration ranged from 4 to 24 hours, depending upon the temperature.

Relative settling rates were established by making a slurry of approximately 30 g/L of the oxide powder in sodium aluminate solution No. 2 (see Table II) and measuring the rate of fall of the particles. No flocculants were added to the solution. The temperature was maintained at 90°C.

Results

I. Settling Rates

Relative settling rates, as functions of particle size and surface area, for goethite and hematite are shown graphically in Figure 1. Within the confines of the experimental range the settling rate of goethite increases with increasing particle size (decreasing surface area) whereas that of hematite appears to be independent of both particle size and surface area. For any given particle size, the settling rate of hematite is considerably greater than that of goethite. This large difference of settling rates cannot be accounted for solely on the basis of the small difference in specific gravity of the two phases.

Also compared were settling rates of hematite prepared by the transformation of the α-FeOOH phase to α-Fe₂O₃ (see Figure 2). The transformation of goethite to hematite can be achieved in two ways: 1) by thermal dehydration in air in a temperature range of 300-550°C (96 hours) and 2) by hydrothermal treatment (in Na₂O/Al₂O₃ solutions) at tem-

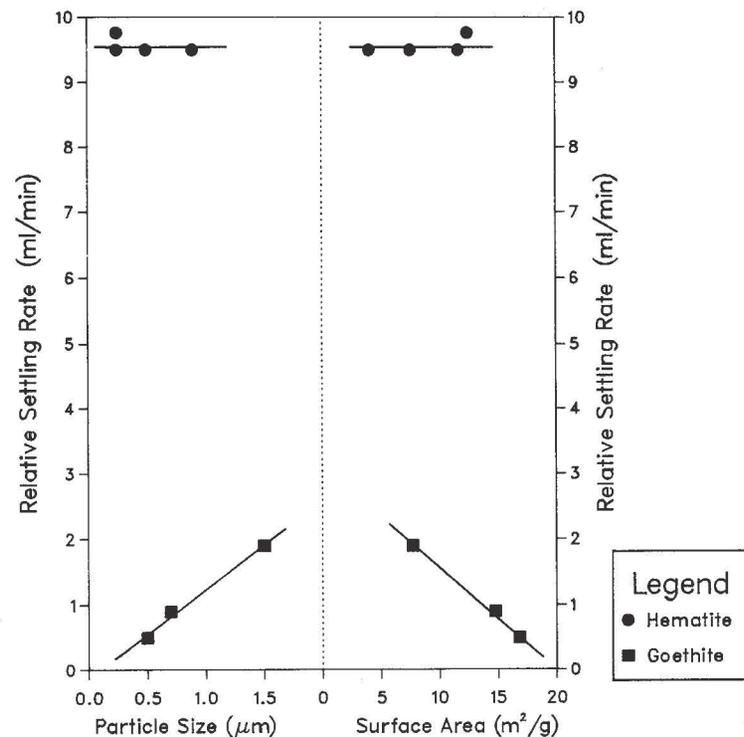
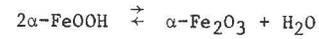


Figure 1 - Relative settling rates of iron oxides.

peratures above 175°C (1). The transformation in air proceeds without a change in morphology of the original goethite particle, but leads to an increase (3-4 fold) in specific surface due to porosity caused by a loss of approximately 10% of the particle mass:



Hydrothermal transformation on the other hand proceeds via dissolution and reprecipitation steps and thus results in a change of crystal shape and size distribution (see Discussion Section). Electron micrographs of these iron minerals are shown in Figures 3 and 4.

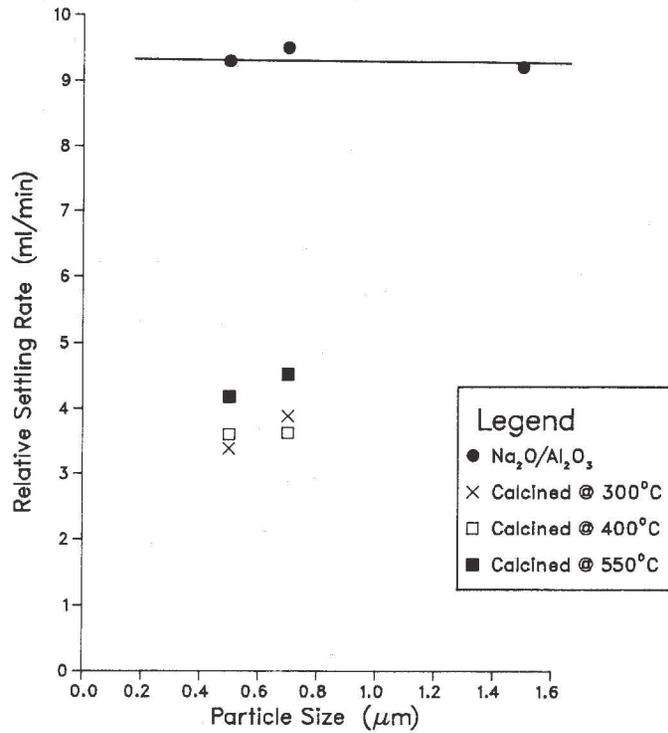


Figure 2 - Relative settling rates of treated goethite.

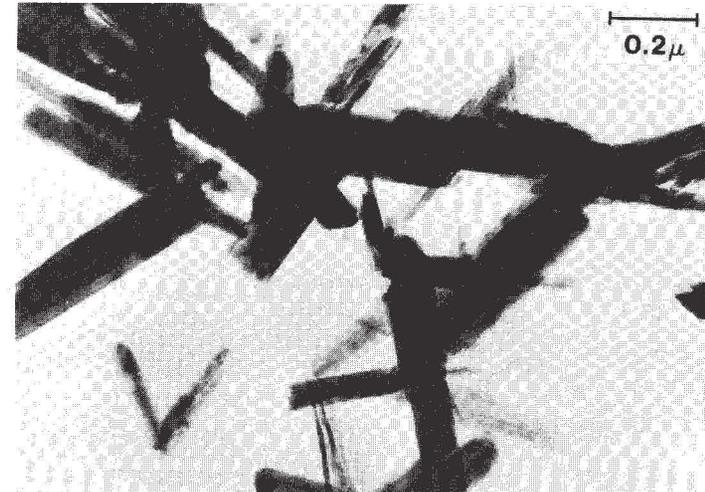


Figure 3 - TEM micrographs of (a) goethite, and (b) goethite calcined at 400°C.

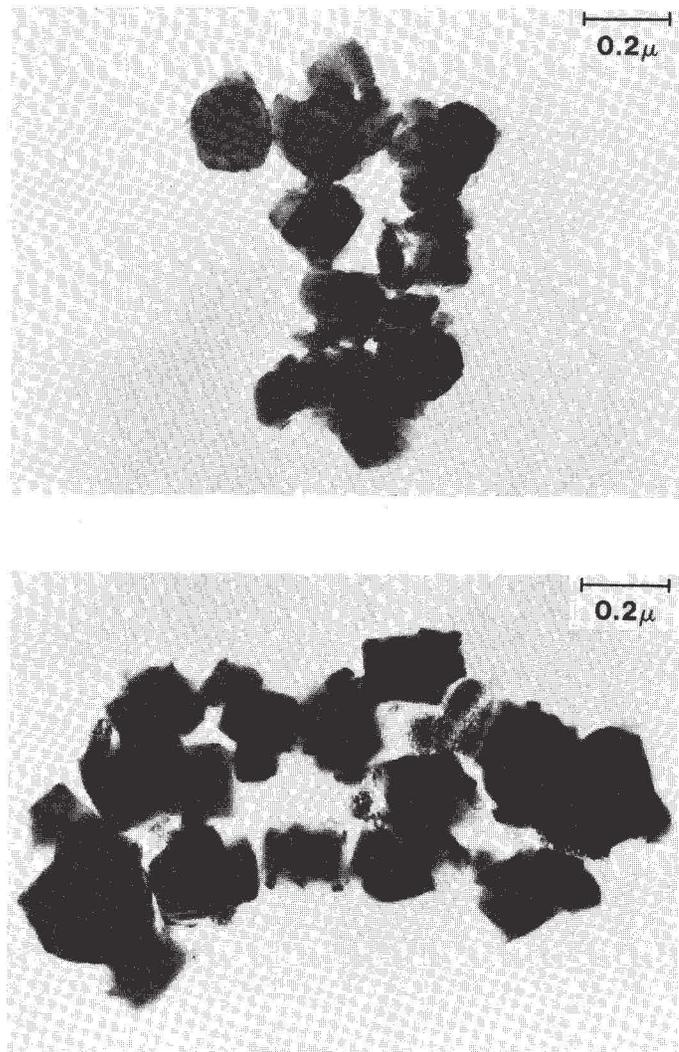


Figure 4 - TEM micrographs of (a) hematite and (b) hematite formed via hydrothermal transformation of goethite.

The XRD pattern for the hematite obtained via thermal dehydration reveals a few sharp and some diffuse lines, thus indicating a degree of lattice disorder of the newly formed hematite. Thermal treatment of goethite results in approximately 55, 60 and 80% transformation to crystalline hematite at temperatures of 350, 400, and 550°C, respectively. This was determined by a comparing peak areas of selected diffraction peaks against a standard of pure, crystalline hematite.

II. Transformation Isotherms

Series A (pure goethite) and Series B (goethite and hematite) isotherms for the hydrothermal transformation of goethite to hematite are illustrated in Figures 5a and 5b. The 225°C and 250°C Series B isotherms are not shown because transformation was too rapid to be measured (100% within the first one-half hour).

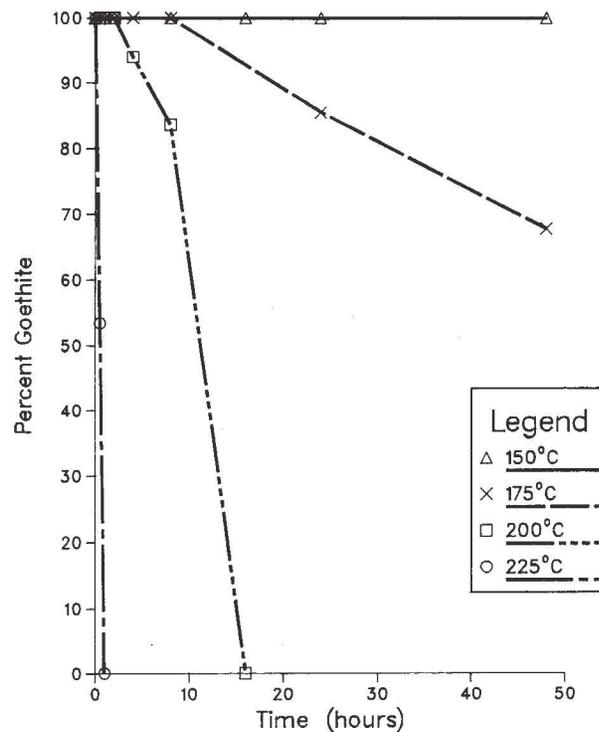


Figure 5a - Transformation isotherms for goethite (Series A).

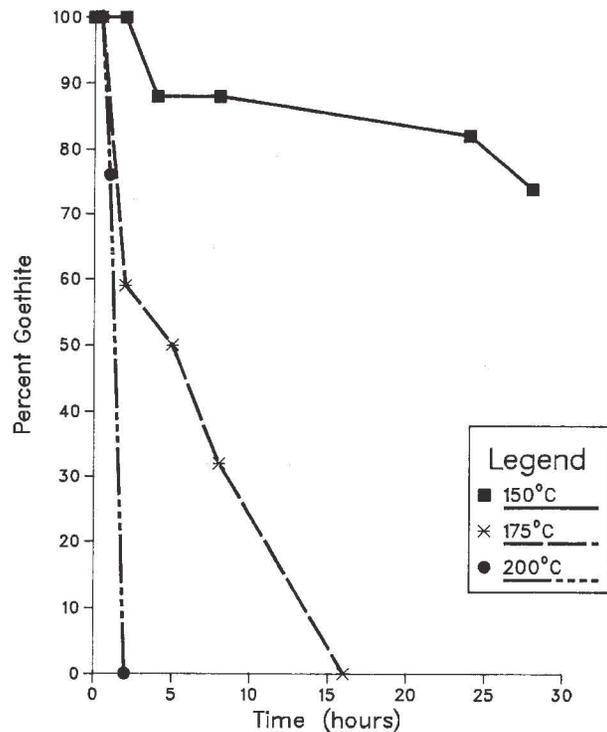


Figure 5b - Transformation isotherms for goethite/hematite mixture (Series B).

Transformation rates at 175°C in several solutions of varying $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ concentrations are plotted as a function of free Na_2O in Figure 6. The equilibrium solubility of Al_2O_3 in Na_2O solutions at 175°C is approximately 1 mole $\text{Al}_2\text{O}_3/1.2$ mole Na_2O (7). The free Na_2O concentrations were calculated accordingly. For a given free Na_2O concentration the transformation rate in pure Na_2O solutions is greater than in sodium aluminate solutions.

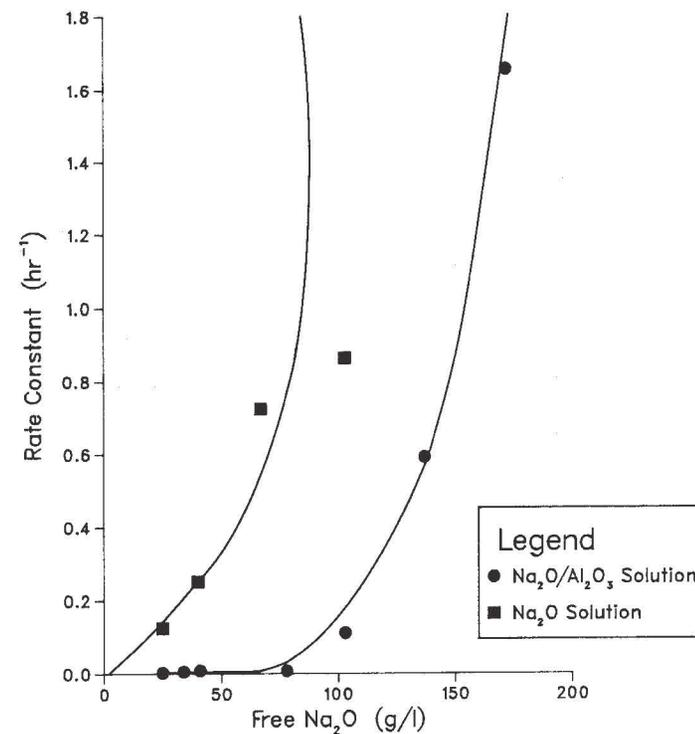


Figure 6 - Iron mineral transformation rates as a function of free Na_2O .

III. Solubility of Goethite in Sodium Aluminate Solutions

Values for equilibrium solubility of $\alpha\text{-FeOOH}$ in sodium aluminate solutions with the Na_2O and Al_2O_3 concentrations ranging from 150-250 g/L and 62-103 g/L, respectively, are represented as a function of temperature in Figure 7. The solubility curves exhibit an exponential increase with temperature, the equilibrium solubility being close to zero at room temperature. Solubility was also noted to be a function of solution composition. The correlation between equilibrium solubility and concentration of free Na_2O is represented in Figure 8. At a given concentration of free Na_2O , the isothermal solubility of iron is considerably greater in the sodium aluminate solutions than in the pure NaOH solutions.

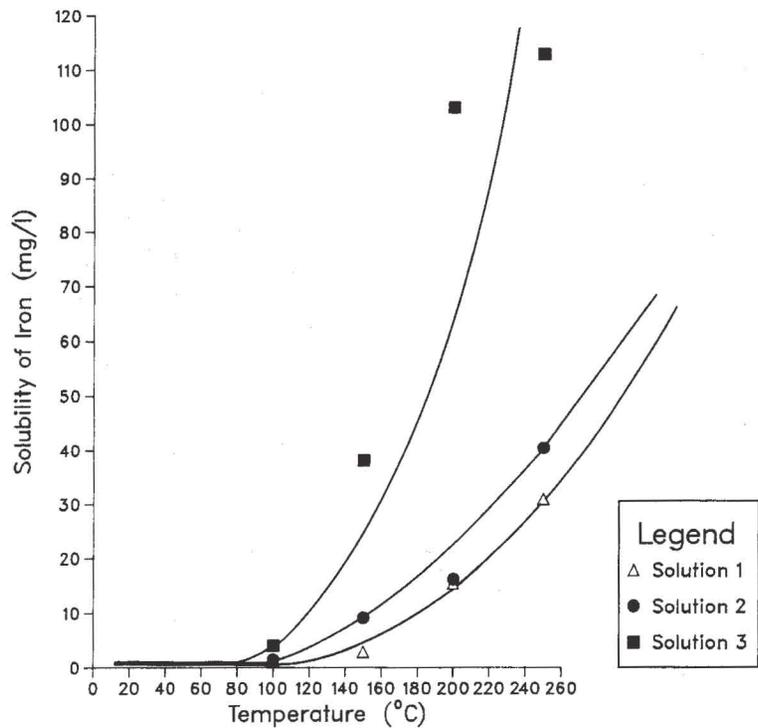


Figure 7 - Solubility of iron in caustic as a function of temperature.

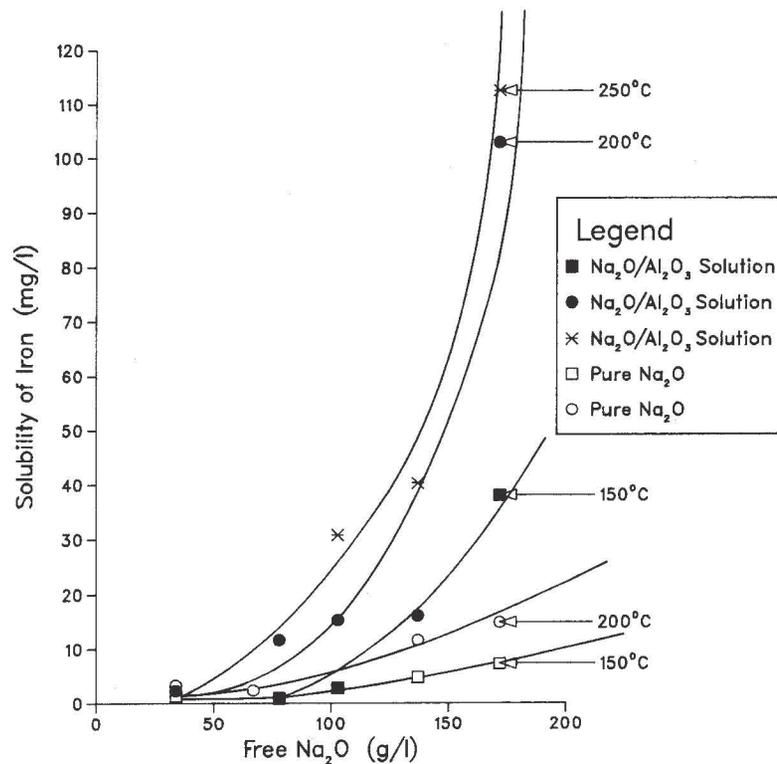
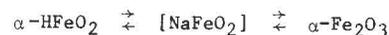


Figure 8 - Solubility of iron in caustic as a function of free Na₂O.

Discussion

This investigation has confirmed the relation of settling rate to type of iron mineral. For a given particle size and surface area, hematite exhibits considerably faster settling rates than goethite. In the realm of random motion, the acicular goethite particles tend to have a greater collision probability owing to the larger mean diameter of the particles. In spite of this, the agglomeration tendency of the α -FeOOH particles is much lower. The difference in settling behavior can, therefore, be attributed to a difference in surface properties of the two minerals. The surface properties of goethite are such that they do not allow for the strong particle-particle interaction necessary for flocculation. The exact nature of the goethite surface has yet to be determined. The transformation of goethite to hematite, hydrothermally or via calcination leads to an alteration of the FeOOH surface properties and results in a considerable increase in settling rates (see Figure 2). As mentioned in the previous section, the hematite obtained by thermal transformation of goethite is not completely converted to crystalline hematite. Although settling rates and % transformation are seen to increase with increasing calcination temperatures, the rates are relatively slower than those obtained for hydrothermally converted hematite. Since there is no linear correlation between the percentage of crystalline hematite and the settling rate, one has to assume an effect of particle shape. The isometric hematite particles obtained after hydrothermal transformation of goethite tend to pack tighter, forming denser flocs that settle rapidly. A certain degree of randomness is expected in the packing of the acicular hematite particles (from calcination) during floc formation. Hence, the flocs formed are less dense, more voluminous, and settle relatively slower.

In the pure system $\text{Fe}_2\text{O}_3/\text{H}_2\text{O}$, hematite is the thermodynamically stable phase at temperatures greater than 343 K. The change in Gibbs free energy (ΔG_{343}) for the transformation of goethite to hematite is approximated at 2 kcal/mole (4). Since this represents a relatively weak driving force, the chemical environment is more likely to control the species that will be present in the system. The high caustic concentrations encountered in the Bayer liquors favor the formation of α -FeOOH. With an increase in temperature the rate of dissolution of the metastable goethite increases rapidly and leads to the formation of a solute species believed to be sodium ferrate (5). At high temperatures, the dissolved species precipitates as α - Fe_2O_3 :



The overall reaction, therefore, consists of two steps: 1) dissolution of goethite and 2) precipitation of hematite.

The reaction can proceed in either direction, the direction and rate being determined by the experimental conditions. Under high caustic concentrations and low temperatures, the α -FeOOH will precipitate in the same form as long as solid hematite is absent. This effect is illustrated in the 150°C Series A isotherm (see Figure 5a). The energy of activation (E_A) calculated from an Arrhenius plot, for this system, is approximately 50 kcal/mole. The transformation rates achieved at temperatures greater than 175°C suggest that under such conditions the system has sufficient thermal energy for spontaneous nucleation of hematite. In the presence of hematite seed, as in the case of Series B isotherms (see Figure 5b), the E_A is reduced to approximately 23 kcal/mole. The additional E_A (27 kcal/mole) for System A corresponds to that required for spontaneous nucleation.

For a given concentration of free Na_2O , the transformation rates in pure Na_2O solutions far exceed those in sodium aluminate solutions (Figure 6). The effect of Al_2O_3 in solution on the rates is not completely understood. Transformation being dependent upon dissolution rates, it should be pointed out that the dissolution of goethite in sodium aluminate solutions represents the reaction of FeOOH in the quaternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$, which is quite different from that in the ternary system $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$. It is very likely that the dissolution of Fe^{3+} in the quaternary system results in the formation of a solute species different from NaFeO_2 -- a solute species possibly bearing Al and Fe cations. The presence of a solid solution of aluminum in α -FeOOH (aluminous goethite) is well documented. The limit of substitution of Al^{3+} in FeOOH is reported as high as 33% (mole) (6), while others claim that the limit of true isomorphous substitution is on the order of 10-12 mole % and that higher concentrations of Al^{3+} are due to epitaxial intergrowth of α -AlOOH on α -FeOOH. One can assume that the observed higher solubility of Fe^{3+} in the quaternary system represents the equilibrium between solid α -(Fe,Al)OOH and the solute species which is different from the $\text{Fe}^{3+}/\text{FeOOH}$ equilibrium in the ternary system $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$. The solubility of Fe^{3+} in the quaternary system is therefore intermediate between that of the pure ternary boundary systems: $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, the solubility of the latter (Al_2O_3 in Na_2O solution) being about 2 to 3 orders of magnitude greater. The same argument can be used to explain the increase in transformation temperatures in going from one boundary system to the other with the AlOOH to Al_2O_3 transformation occurring at temperatures between 320-360°C, depending upon the Na_2O concentration (8). The expected transformation temperature for the (Fe,Al)OOH/ Na_2O system would be intermediate between the temperature required for FeOOH to Fe_2O_3 conversion (70°C) and that for the AlOOH to Al_2O_3 transformation (>300°C). Evidence of this effect has been reported in literature (2,3,9), whereby relatively high transformation temperatures (250°C) and slow rates are noted for the conversion of aluminous goethite to hematite.

As seen in Figure 7 the solubility of Fe exhibits an exponential behavior as a function of temperature. This characteristic of the curves suggests that reprecipitation of the iron dissolved during the digest can occur during clarification or precipitation, since these steps are conducted at successively lower temperatures. It is very likely that the iron reprecipitates as fine particles of α -FeOOH because the species is kinetically favored owing to the high caustic concentrations and the presence of hydroxylated surfaces acting as nucleation sites.

Conclusions

Based on the foregoing discussion, one can conclude that clarification is affected by the particular iron mineral phase present in the system. Due to its surface properties, goethite can lead to slow settling rates in pure sodium aluminate solutions. Clarification properties can be enhanced by modification of the goethite surface such as in the transformation of goethite to hematite, which settles considerably faster. Under the low temperature Bayer digest conditions, very little or no transformation is realized for several reasons: low temperature, short digest time, lack of sufficient hematite nucleation sites, and liquor components that may be detrimental to the reaction. Clarification problems can be further complicated by reprecipitation of the iron dissolved during the digest.

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References

1. D.K. Grubbs, S.C. Libby, J.K. Rodenburg, and K. Wefers, "Clarification Properties of Jamaican Bauxites," J. Geol. Soc. Jamaica, Proc. Baux. Sym. IV, June 1980, pp. 176-186.
2. B. Schepers, "Optimizing the Digestion of Bauxites of Different Mineralogical and Chemical Composition," Erzmetall, 29(2) (1976) pp. 61-66.
3. K. Solymer, Matyasi, and B. Toth, "Digestion of Hungarian Goethite Bearing Bauxites with Additives," Banyaszati es Kohaszah Lapok - Kohaszah, 110(5) (1977) pp. 219-224.
- 4a. K. Wefers, "The System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$," Metall, 22 (1968), pp. 224-228.
- 4b. K. Wefers, "The System $\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$," Ber. Deutsch Keram. Geo., 43 (1966), pp. 677-684, 703-708.
5. J.J. Kotte, "Bayer Digestion and Predigestion Desilication Reactor Design," pp. 45-79, in Light Metals, G.M. Bell, ed., TMS-AIME, Chicago, Ill., 1981.
6. D.C. Golden, "Physical and Chemical Properties of Aluminum-Substituted Goethite," Ph.D. Thesis, North Carolina State University, Raleigh, N.C., 1978.
7. K. Wefers, "Phase Relationships in the System $\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$," Erzmetall, 20 (1967) pp. 19, 71.
8. K. Wefers, "The System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$," Metall, 21 (1967) pp. 422-431.
9. N. Brown and R.J. Tremblay, "Some Studies of the Iron Mineral Transformations During High Temperature Digestion of Jamaican Bauxite," pp. 825-839, in Light Metals 3, Helge Forberg, ed., TMS-AIME, Dallas, Tex., 1974.