Solubility Behavior of Titanium(IV) Oxide in Alkaline Media at Elevated Temperatures

S. E. Ziemniak, 1 M. E. Jones, 1 and K. E. S. Combs 1

Received February 12, 1992; Revised February 5, 1993

A platinum-lined, flowing autoclave facility was used to investigate the solubility behavior of titanium dioxide (TiO₂) in aqueous sodium phosphate, sodium hydroxide and ammonium hydroxide solutions between 17 and 288°C. Baseline Ti(IV) solubilities were found to be on the order of one nanomolar, which were enhanced by the formation of anionic hydroxo- and phosphato-complexes. The measured solubility behavior was examined via a titanium(IV) ion hydrolysis/complexing model and thermodynamic functions for the hydrolysis/complexing reaction equilibria were obtained from a least-squares analysis of the data. The existence of three new Ti(IV) ion complexes is reported for the first time: Ti(OH)₄(HPO₄)⁻², Ti(OH)₅(H₂PO₄)⁻² and Ti(OH)₅(HPO₄)₃⁻. The triply-charged anionic complex was the dominant Ti(IV) species in concentrated, alkaline phosphate solutions at elevated temperatures. This complex is expected to exhibit C.N. = 4 (i.e., Ti(OH)₂OPO₄²⁻). A summary of thermochemical properties for species in the systems TiO₂-H₂O and TiO₂-P₂O₅-H₂O is also provided.

KEY WORDS: Titanium(IV) oxide; rutile; aqueous solutions; metal ion hydrolysis; phosphatocomplexing; equilibrium constant; thermodynamics; pressurized water; hydrothermal solutions; corrosion.

1. Introduction

Throughout approximately 100 years of the steam power industry’s history, copper and iron alloys have been used in tubing for main steam condensers. In the 1970's, titanium tubes were first employed in power plant condensers to resolve specific corrosion concerns. Power plants in the United States and other countries are currently switching to titanium in an effort to increase the leaktight integrity of condensers cooled with seawater or brackish water and simultaneously remove copper-bearing materials from the condensate system. 

In order to quantify the hydrothermal aspects of the titanium...
oxide corrosion film that subsequently forms on this material, \textit{a priori} knowledge of its phase stability and solubility behavior must be available. Present knowledge regarding a titanium dioxide (TiO$_2$) constituent is practically nonexistent; the hydrolysis behavior of Ti(IV) is known reliably only at room temperature over a limited pH range.$^{(2,3)}$

The present work was undertaken to create experimental and theoretical bases for estimating solubilities of a titanium corrosion product/corrosion film constituent (TiO$_2$) over a broad range of temperature in the presence of various alkaline pH agents. Our methodology involved the pumping of alkaline solutions of known composition through a bed of TiO$_2$ granules and analyzing the emerging solution for Ti. Three different pH-controlling reagents were tested: sodium phosphate, sodium hydroxide, and ammonium hydroxide. Equilibria for the following reactions were described in thermodynamic terms: (a) TiO$_2$ dissolution; (b) Ti(IV) ion hydroxocomplex formation (hydrolysis); and (c) Ti(IV) ion phosphatocomplex formation.

2. Experimental

2.1. Materials

Titanium dioxide (rutile) was prepared from certified reagent titanic oxide (anatase, Fisher Scientific). Because the as-received powder was too fine to be retained as a packed column in a flowing autoclave system, it was transformed into larger particles by compaction (34.5 MPa) followed by attrition through a 10 mesh sieve onto a 20 mesh sieve. The particles were then fired at 1400$^\circ$ for 4 hrs in a flowing oxygen atmosphere and slowly cooled to room temperature. The material produced in this manner consisted of hard, irregular-shaped, pale brown particles with dimensions of 1.3 to 2.5 mm.

Examination of the coarse particles at high magnifications by scanning electron microscopy (SEM) revealed a pebble-grained surface composed of partially sintered (\textit{i.e.}, melted) particles of the original material (see Fig. 1). Density measurements using a mercury pycnometer gave a value of 3.97 g-cm$^{-3}$ (93% of theoretical), indicative of a high degree of sintering. Because these crystals were truly sintered together, the effective crystal size was close to that of the coarsened particle and thus not expected to exhibit enhanced saturation solubility levels.

Although the starting powder was a bright white color, the sintered material was photosensitive, as its surface darkened to pale brown when exposed to light and air on a bench top. This color change is