Chapter I

Introduction

1.1 Motivation, Objective and Scope

Medical and biological investigations (in vivo, small rodents) of natural mineral fibres, including asbestos. Suggest that the carcinogenic risk may depend on the geometry and residence time of inhaled fibres. Although the residence time of fibres is influenced by chemical durability, only few studies were concentrated on this matter. Scholze and Conradt (1987) had formulated a model for the specific case of in vitro corrosion of technical fibrous materials which allowed to calculate the residence time of numerous chemically different man-made mineral fibres (MMMF) in a physiological solution to establish a quantitative durability classification. Moreover, extended experimental in vitro studies on the chemical durability of natural mineral fibres had been performed during the past years. A large number of different fibres was exposed to a simulated extracellular fluid under flow conditions, and the progress of glass corrosion was recorded over extended periods (up to four months). The applied leachant was so-called Gamble's solution, pH $\sim$ 7.6 (see table 3.6). Some tests were also performed at pH $\sim$ 5. Results were presented in terms of fibre dissolution velocities. Until today, more than 50 different fibre species, eventually with binder, had been investigated.

As-received commercial products were included as well as model fibres of systematicly varied composition.

In order to complement these investigations, a study based on thermodynamics and kinetics theory to establish a predictive model able to predict some relation between the dissolution velocity and the chemical composition of fibres was performed. The objective of the experimental work was the direct gravimetric determination of dissolution velocities of monolithic glass samples with compositions typical of MMMF products. This work was designed to confirm results received from experiments with fibres so far. Along with this, the effect of binder, CO_2 phosphate and pH value, on the dissolution velocities of the different types of glasses was also demonstrated.

Scope of thesis work

Two parts of the thesis work are to be distinguished. Firstly, a data base in terms of speciation of glass and speciation of aqueous species was prepared, based on thermodynamics and kineties theory, using Lotus 123 as a calculation worksheet. After that, a predictive model was established. Eight different glass types were used to calculate dissolution Gibbs free energy from the model. Some materials investigated earlier (Scholze and Conradt, 1987) were also compared. Secondly, experimental work was performed to determine glass dissolution velocities (see the following flow chart of experiments). Some conditions were selected to comply with the equipment of the glass lab such as, direct gravimetric determination, simple sample geometry (chip sample) or replenishing solution. Besides this, some further effects were also investigated. The following flow chart shows the scope of thesis work.

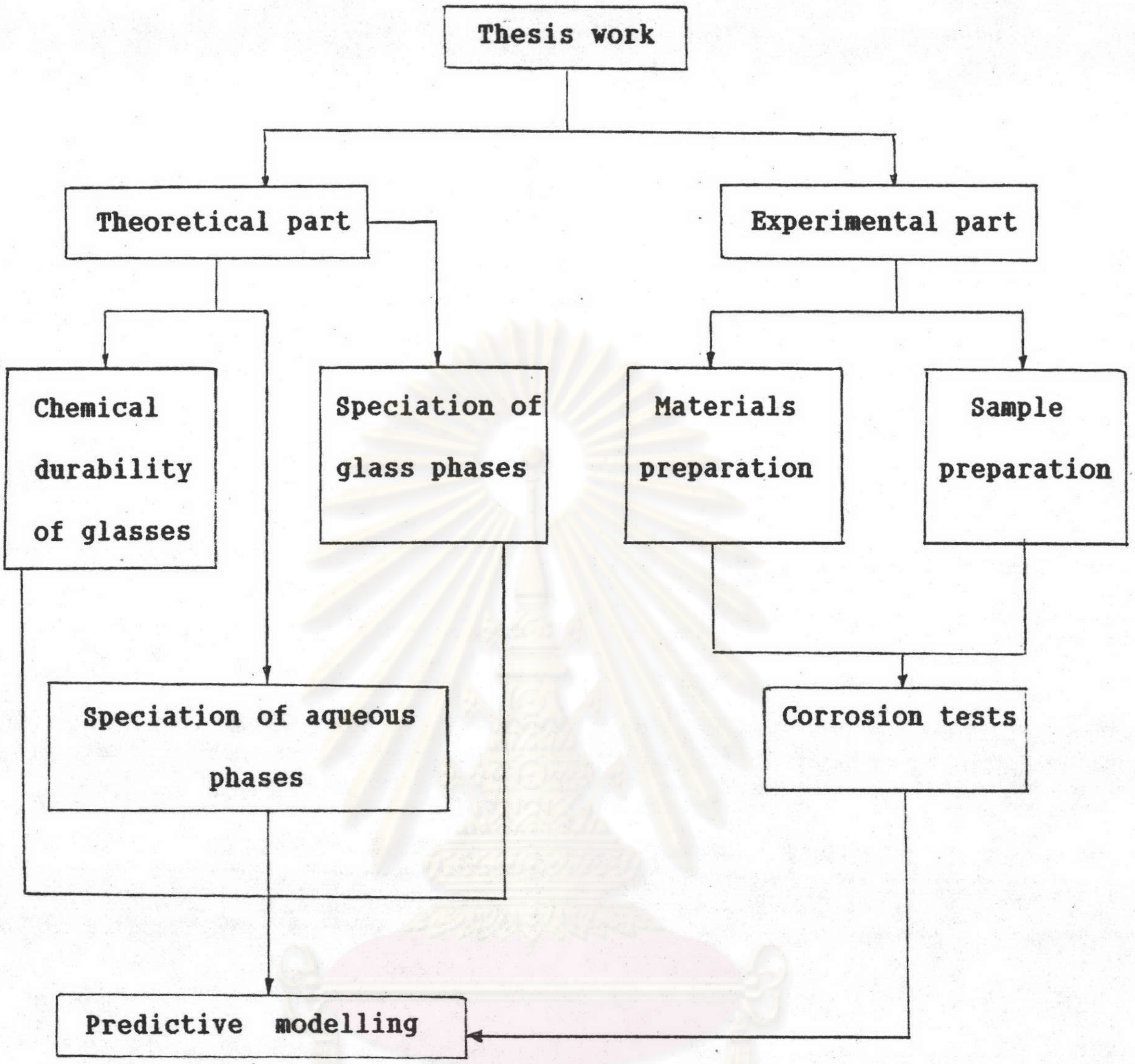

Fig. 1.1 Flow chart of thesis work.

1.2 <u>Liturature Survey</u>

Until today, an accurate quantitative description of the glass corrosion process is still not posible. Beside the many excellent results on the details of glass corrosion (which cannot be quoted here because of their large number), special reference is made to the so-called thermodynamic approach. This approach was first initiated by

Paul (1982), and further elaborated by Jantzen & Plodinec (1984), Grambow (1985) prefected the issue of aqueous speciation and derived a general equation for glass dissolution. Meanwhile, Conradt, Roggendorf and Ostertay (1985,1986) concentrated on the proper speciation of the glassy phase, which until then, had been over-simplified to metasilicates and free silica. All of the above authors developed systems, which allow at least a semiquantitative classification of the chemical durability of glasses under certain corrosion conditions. As an example, a figure below shows the relation between the corrosion rate $r_{3.0}$ under static conditions and the Gibbs free energy of hydration of different glasses designed for radioactive waste disposal. The index 3.0 denotes the product of corrosion time t and the ratio s = glass surface area per leachant volume, i.e., s.t = 3.0 cm^{-1}. Predicting fibre durabilities under flow conditions is not any less different. This is because, firstly, the corrosion rate cannot be measured directly but has to be corrected for the influence of fibre geometry. Secondly, the major amounts of glass in the experiments are no real bulk material (which can be described in terms of bulk properties) but surface-near material.

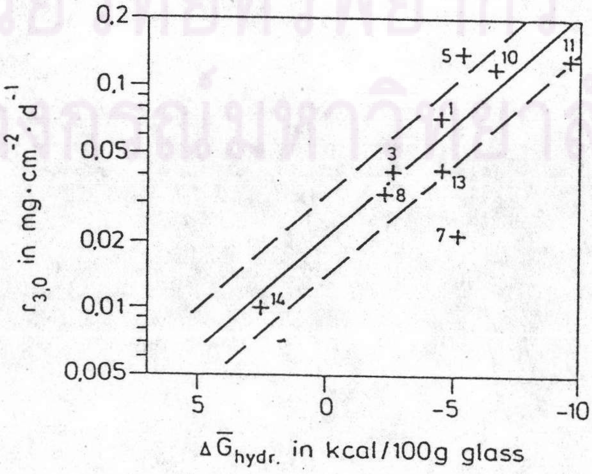

Fig. 1.2 Corrosion rate versus dissolution Gibbs free energy.