An apparatus for the study of fast precipitation reactions

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Abstract

An apparatus is described for the measurement of the rates of fast precipitation reactions. It consists of a T-tube, where reactants are added to the arms of the T, mixed rapidly at the junction, and the rates of disappearance of reactants or appearance of products are measured along the stem of the T. The geometry of the system results in a steady state being established in the apparatus, enabling detailed analysis of reaction progress. The apparatus has been used to investigate the kinetics and mechanism of iron sulphide precipitation reactions. It has enabled measurements to be made with relatively high precision and good accuracy of the first 130 ms of reaction time.

KEYWORDS: reaction kinetics, precipitation, iron sulphide.

Introduction

HETEROGENEOUS reaction kinetics, particularly the interrelationships of solids and solutions, are key factors in the study of the rates and pathways of natural processes. Considerable progress has been made in the studies of the kinetics and mechanisms of geochemically-significant dissolution processes. A number of innovative techniques have been introduced to define the hydrodynamics of the reacting systems, such as the spinning disk technique (Rickard and Sjoberg, 1983) and the fluidized bed approach (Chou and Wollast, 1984). At the same time detailed studies of microscopic reaction space have been introduced, using techniques such as XPS, Auger, and Rutherford electron scattering.

In contrast, studies of precipitation kinetics have not been so widely featured in recent geochemical literature. The major technical problems in this area centre on the problems of defining the initial precipitate produced. Ostwald (1897) first studied precipitation processes in highly supersaturated solutions and developed one of his interminable 'rules' (sometimes called 'The Law of Successive Reactions'). Basically this described his original observation that the first phase precipitated from a solution was not the stable end-member, but a metastable intermediary. This observation implies that, in order to understand the pathways of precipitation processes, early reaction time must be accessed in a controlled manner. This is because the initial precipitate formed may be ephemeral and determine the subsequent homogeneous solid–solid pathway to more familiar species. In this paper, I describe a technique for accessing the early reaction time of precipitation reactions and apply this specifically to rapid sulphide precipitates.

Apparatus

The apparatus is outlined in Fig. 1. Basically it consists of a glass T-tube. The junction of the T is a millisecond mix: a small glass sphere with the entrances from the arms of the T tangential on opposite sides of the bowl and the exit to the stem of the T perpendicular to these. Reactant solutions are pumped into the arms of the T, mixed in the millisecond mix and the product solutions exit via the stem of the T. It is obvious that the distance along the stem of the T is a measure of reaction time; it is equally obvious that the system is in steady state, and any point along the stem remains constant for the duration of the experimental run.

The glass tubing used in the apparatus consists of thick walled 1.8 mm bore pyrex glass capillary. The capillary has two advantages: (1) it reduces the amount of stock solution required to complete a run and (2) it enables short reaction times to be accessed.

The pump employed was a peristaltic pump with no measurable pulsation. It delivered a maximum 10 cm^3 solution in 17.57 s or 570 $mm^3 \cdot s^{-1}$. Mixing in the millisecond mix was complete within 20 ms and the tube stem of 20 cm represented a total 810 ms of reaction time.

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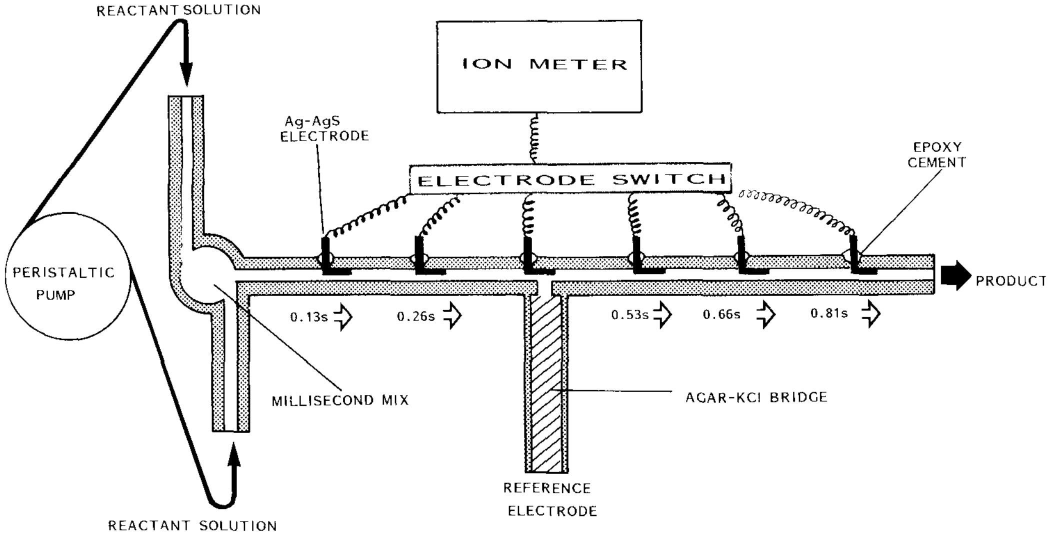

FIG. 1. The T-tube design for studying fast precipitation reactions. The gross dimensions of the standard T-tube are to scale, although the dimensions of the glass tubing itself are exaggerated. The tubing is 0.6 cm o.d. with a capillary bore of 1.8 mm. The microsecond mix at the junction of the T has an internal radius of approximately 2 mm.

Measurements along the tube were made by silver–silver sulphide electrodes cemented into the tubes at intervals. The first electrode was 28 mm along the tube, and represented 130 ms of reaction time. The silver–silver sulphide electrodes were simply pieces of silver wire bent downstream in the tube and soldered to platinum wire and copper wire leads into an Orion multielectrode switchbox and amplified in an orion EA920 ionmeter. The reference electrode was connected to the centre of the stem of the T-tube via an agar-KCl bridge.

Methods

All reactant solutions were made up with deoxygenated distilled water and kept under O_2-free nitrogen. The tube and electrodes were routinely cleaned with HCl and washed out with the distilled water. Runs were initiated by standardizing the electrode responses with solutions of known sulphide concentration prepared with weighed amounts of p.a. grade sodium sulphide. The process was repeated before and after runs, thereby eliminating problems with the simplicity of electrode manufacture.

Experimental runs were performed by pumping metal and sulphide solutions through the T-tube at equal rates and measuring sulphide decrease with time along the tube. The products were collected at the outflow and analysed by XRD, UV-VIS spectrophotometry and analytical SEM. The reaction products are not the precipitates after short reaction times. To date, I have found no way of collecting these initial precipitates; they are highly dispersed and not easily visible and they pass readily through a 0.2 micron Millipore filter.

Results

The major uncertainties in the experimental design centred on the electrode systems. There was some initial concern about (i) junction potentials, (ii) streaming potentials, and (iii) electrode fouling. In fact, the standardization method used eliminated these problems in practice. Even so, absolute electrode potentials were found to be repeatable even after long periods, suggesting that at least junction and streaming potentials represented no major problem. In fact the latest measurements of pK_2 of H_2S (Schoonen and Barnes, 1988; Giggenbach, 1971) mean that the sulphide ion, S^{2-}, does not exist in aqueous solution and earlier theories of how the silver–silver sulphide electrode worked are untenable. It appears that the system used in this experimentation functions adequately as a sulphide electrode.

Electrode fouling is a more serious problem. However, no blockage due to precipitation was observed during the experimentation, probably as a result of the highly dispersed nature of the initial precipitate. Furthermore, standardization at the beginning and end of runs revealed no problems with iron and zinc solutions. In contrast, copper solutions appear to have a strong fouling effect on the electrodes, and this constrains the conditions under which copper sulphide kinetics can be studied.

In standardization runs the electrodes showed linear response from 10^{-1} to 10^{-7} mole dm^{-3} total dissolved sulphide. Repeated runs showed a reproduceability of ±1 mV over this range, which is well within 1%.

The accuracy of the results was affected by sulphide concentration, pH control and electrode response. The rate of electrode response was no problem, because the system was in steady state. However, the fraction of sulphide removed from solution was not only a measure of reaction rate but also the relative amount of dissolved metal added. For example, for monosulphides, if the concentration of the dissolved metal was two magnitudes less than the dissolved sulphide, a maximum of 1% decrease in concentration of sulphide could be observed in an ideal case.

The reaction of protonated sulphide species with metals results in a substantial decrease in pH. For repeatable sulphide concentration measurements the solution must be buffered. Since the amount of proton release is at least equivalent to the concentration of the dissolved sulphide species, large amounts of buffer solutions (usually phosphate based in the pH range of interest) must be added. The success of the pH control then has a significant effect on the results. In a new series of experiments, it is intended to let the pH vary and record this variation through the tube by means of micro-pH electrodes placed opposite the silver–silver sulphide electrodes.

Thirdly, reaction rates with iron sulphides were found to be highly dependent on sulphide concentration. At high total dissolved sulphide concentrations the rate was so fast that it could not be measured. The same situation pertained when the dissolved sulphide concentration fell below 10^{-7} mole dm^{-3}.

In summary, the accuracy of the results has been estimated to be ±10% relative. As shown below, however, it is probable that the real accuracy is at least a magnitude better than this in most cases. In fact, because of the surprising complexity of the concentration–time curves, I have been most sceptical about the accuracy of the measurements. However, repeated experiments involving, for example, change of flow rate so that particular reaction times are at different electrodes, or varying flow rates with the whole of the reaction measured at a single electrode, reveal remarkable consistency.

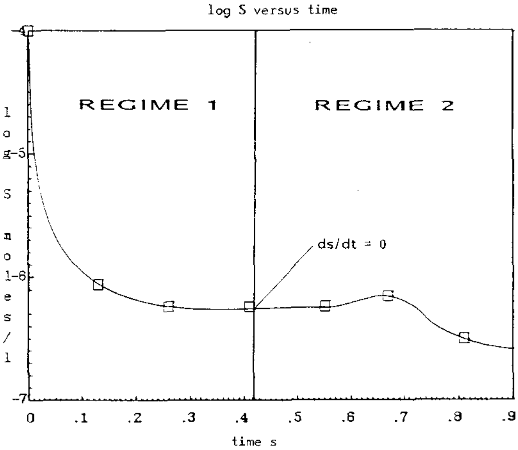

FIG. 2. Typical concentration–time curve derived for the precipitation of iron(II) sulphide from aqueous solution at 18° C. The curve suggests concurrent reactions where precipitation dominates in Regime 1 and re-reaction with the solution becomes relatively important in Regime 2.

Discussion

A typical concentration time curve for the reaction between dissolved iron (II) salts and dissolved sulphide is shown in Fig. 2. The curve is characterized by an exponential decrease in sulphide concentration in the initial stages of the reaction. Usually some 90% of the reaction is complete in the first 260 ms. This is followed by a small increase in dissolved sulphide, before the curve approaches a constant value. This increase on the curve is real. It is repeatable and has been checked several times. It is interpreted (cf. Rickard, in prep) as indicating the re-reaction of the initial precipitate with the solution to form the more familiar amorphous FeS. This reaction has been proposed by Kornicker (in Morse *et al.*, 1987). It is important, since it suggests that the initial phase formed is not amorphous FeS, but some precursor phase with a lifetime of less than 400 ms. The results may cast some light on to the nature of nucleation and precipitation and the origin of Ostwald's 'Law of Successive Reactions'. It is possible (and at least kinetically probable) that the earliest precipitates are not ordered materials, but disordered gels not much different from the solution from which they derived. Ostwald in fact postulated that the first-formed phase would be that having a free energy closest to that of the system in solution. It may be that continued study of extremely early reaction times in precipitation processes may reveal much about the nature of the process involved in this change of state.

Conclusions

The kinetics of the fast precipitation reactions can be investigated using the steady state, T-tube technique. The technical problems of electrode reaction times, junction potentials, streaming potentials and blockage are overcome through the apparatus design and repeated standardization.

At present, the first 130 ms of reaction can be accessed. It is intended to install a bigger pump to access the first 10 ms of reaction. The pumps tested to date, however, although having the required delivery rates and pressure gradients, tend to provide a pulsed flow. If this problem can be overcome, I see no reason why even earlier reaction times cannot be achieved.

The measurement techniques are not limited to silver–silver sulphide electrodes and we are already testing micro-pH electrodes in this system. Because of the steady state nature of the apparatus, response times of pH electrodes are no problem. This suggests the possibility of broadening the experimentation into other, non-sulphide systems. It appears that this type of apparatus may have wide application in the investigation of geological reactions because of the analogy in its design to many natural fluid systems.

Although we are unable to capture the earliest precipitate at this time, I suspect that this may not be a serious problem. It is possible that the earliest precipitate is not much bigger that the critical nucleus. As such it should be amenable to spectroscopic methods of investigation. The design of the capillary tube has an ideal geometry for laser Raman techniques and Fe–S and Fe–HS should be highly polarized.

Acknowledgements

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