

Scale up production of nanoparticles using hydrothermal synthesis

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ABSTRACT

Supercritical water hydrothermal synthesis of metal oxide nano-particles is a relatively simple and 'green' process. However, the technique has not yet achieved wide scale application at an industrial level. Two issues have stood in the way of progress. Firstly, poor mixing in the reactor, which causes blockages; secondly the scalability of the reactor for high volume throughput. Poor control over the mixing of supercritical water with aqueous metal salts will result in poor process reliability and therefore poor product reproducibility.

This paper compares various reactor geometries to find an optimal design which avoids particle accumulation during scale up. Three particular phenomena were frequently observed at lower flow rates, namely: *fluid partitioning*, *back mixing* and *stagnation*. Faster flow rates can create other problems during the mixing process which can also prove to be problematic during continuous operation. At high flow rates, the nozzle reactor appeared to be able to mix rapidly and continuously indicating that it has commercial potential for nanoparticle manufacture.

Keywords: scale up, hydrothermal, reactor geometry, reaction engineering, mixing.

1 INTRODUCTION

Scale up and scale out of nanomaterial manufacturing techniques is a high priority for those seeking success at an industrial scale. Supercritical water hydrothermal synthesis (scWHS) of nano-particulate metals and metal oxides hold significant promise. The scWHS process is relatively straightforward; it involves mixing an aqueous metal salt stream with supercritical water within a continuous reactor^[1]. The potential for this phenomenon was first exploited for the nano-particle synthesis of cerium oxide by Adschiri and Arai^[2], who showed that under these conditions, hydrolysis of a metal salt was immediately followed by a dehydration step.

Most workers in this area use a T-piece system (Figure 1) where the supercritical water entered the reactor via the side arm, with the aqueous metal salt was introduced through the side arm, the top arm, or horizontally and counter current. Our investigations at Nottingham at using relatively low flow rates, conducted using a T-piece reactor

design were repeatedly hindered by process unreliability resulting in poor product reproducibility^[3]. The non-steady state nature of the process causes particle accumulation and agglomeration within the reactor and, in particular, its two inlets.

- Non-uniform mixing will result in a non steady-state and non-uniform product
- Poor particle transport properties and stagnant zones will result in particle accumulation, and therefore eventual system blockage
- A large reactor residence time will result in undesirable particle growth

2 EXPERIMENTAL PROCEDURE

Observation of fluid mixing through a pressure window is unpractical at high pressures (>220 bar), particularly with the small pipe diameters used in this process. Several reactor designs were investigated using a scaled-up ambient-pressure model (using Perspex, as in Figure 1) to physically recreate the mixing scenario. Methanol and sugared doped water were used to represent the supercritical water and aqueous metal salts respectively, because they exhibit a similar ratio of inertial to viscous forces at ambient conditions to those present in the actual scWHS reactor. The mixing dynamics were enhanced and quantified using a two-dimensional image analysis technique known as Light Adsorption Imaging (LAI). This technique is based on the adsorption of light by a dyed fluid^[4-7], the output being quantitative 'concentration map'.

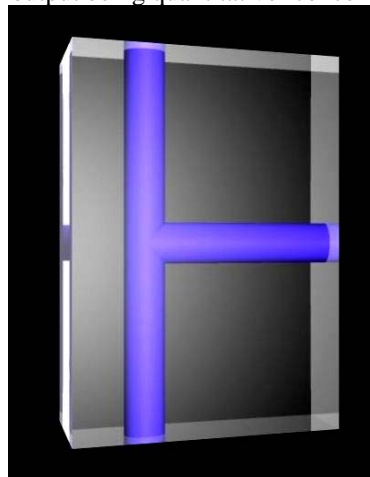


Figure 1: Classic T-Piece Reactor design

3. RESULTS AND DISCUSSIONS

3.1 T Piece Reactors

Figure 2 shows the mixing patterns for the metal salt and supercritical fluid as they are mixed in a vertical T piece reactor. The supercritical water is fed along the side arm of the T-Piece reactor and the metal salt is fed down the top arm. The concentration of supercritical water is marked in red (highest) to light blue (lowest). The metal salt is artificially coloured black. As the flow rate and flow ratio of the two fluids changes, the efficiency of mixing also changes.

At lower flow rates of supercritical water (a), there is significant fluid partitioning and back mixing in the supercritical water inlet. As the flow rate of the supercritical fluid is increased, the partitioning decreases (b). At the ratio of the two fluids reaches an optimum, there is little partitioning or back mixing (c). The potential for stagnation around the upper corner of the supercritical water inlet is difficult to predict. The transition period between (c) and (d) results in some fluid partitioning in the outlet where the metal salt travels down the left side of pipe unmixed. Region (e) is different from the other mixing patterns as ‘roping’ starts to occur in the outlet pipe where mixing is not immediate or steady state. Once the supercritical water flow rate is too high, there is significant back mixing in the metal salt inlet. The challenge with this reactor appears to be in creating a steady state system that can mix instantaneously whilst avoiding roping or fluid partitioning downstream.

Figure 2 : Scale up vertical T piece mixing at higher Reynolds numbers

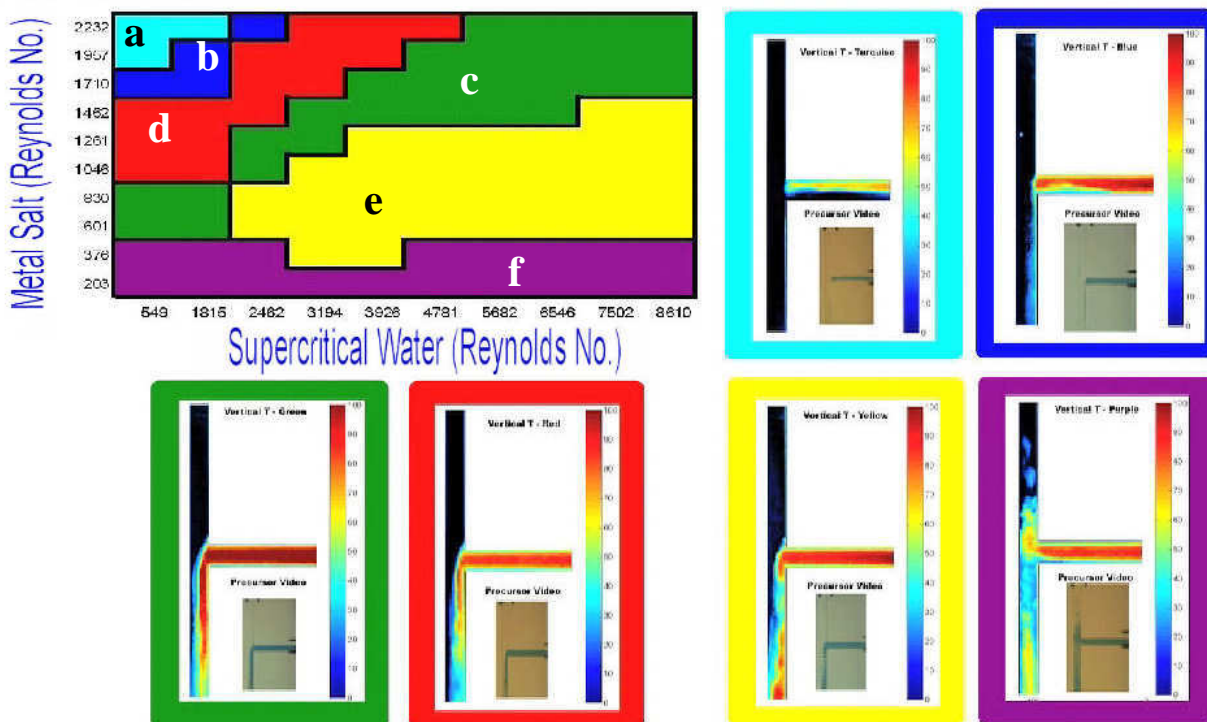


Figure 3 presents the data for the mixing patterns with a horizontal T piece reactor where the two fluids move along the top arms in a counter current arrangement. At high metal salt flows (a-b), there is significant inlet mixing along the bottom of the supercritical water pipe. As the supercritical water flow increases, a non steady state interface is created which moves between the mixing zone and the final section of the supercritical water inlet, with some evidence of fluid roping. The optimal region for mixing occurs with area (c) which reduces the back mixing in either inlet pipe. However, the mixing in the outlet pipe varies considerably over time and does not appear to create very efficient mixing downstream. Regions d-e are more interesting in that the mixing pattern downstream of the mixing zone appear to more controlled but there is some inlet mixing into the metal salt pipe with the creation of an arc interface. Within this interface, there will be micromixing and nanoparticle formation, which could lead to rapid agglomeration of particles and eventual blockages.

As with the vertical T-piece, the challenge with the horizontal T-piece is finding the optimised flow ratio and flow rates to achieve rapid mixing without the potential for slow build up of particles that can be created under non-steady state flow patterns. The non symmetrical nature of the mixing region makes control of particle size and size distribution more difficult.

In light of the difficulties highlighted in Figures 2 and 3, it is not surprising that neither reactor configuration has been successfully commercialized.

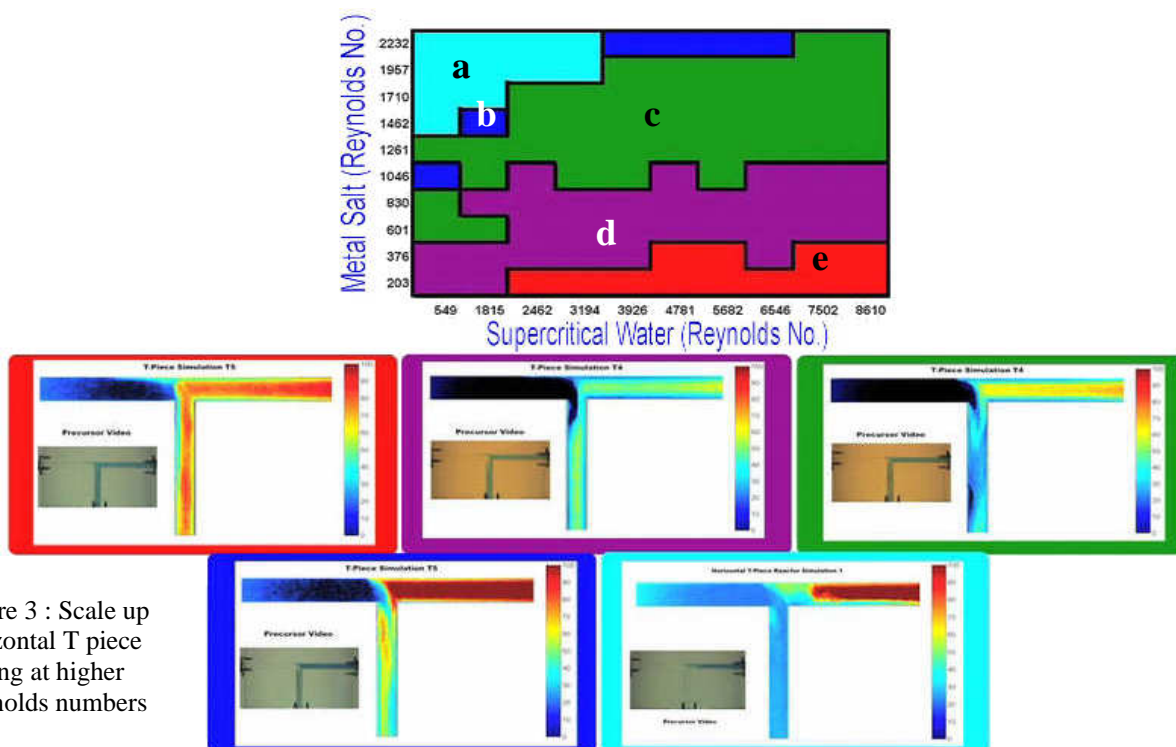


Figure 3 : Scale up horizontal T piece mixing at higher Reynolds numbers

3.2 The Nozzle Reactor

Figure 4a illustrates our patented reactor; it is a pipe-in-pipe concentric arrangement in which the internal pipe has an open-ended nozzle with a cone attached. The supercritical water is fed downwards through the internal pipe and out the end of the 'Nozzle'; the aqueous metal salt steam is fed counter-currently upwards through the outer pipe. The reactor outlet is situated upwards through the outer pipe.

The inner pipe has a nozzle attachment at the end in order to create a thin film interface to facilitate controlled mixing with the upflow of aqueous metal salt. The shape of this interface can be modified to increase the flow rates (and therefore the mixing rates) around the mixing point. An example can be seen in Figure 5. The temperature of the aqueous metal salt prior to the mixing region is $<40^{\circ}\text{C}$. The temperature of the downflow of supercritical water can be varied and so the system can operate at sub-, near- or supercritical conditions. By altering the operating temperature of the system, it is possible to alter the product quality, in terms of yield, particle size and crystallinity. Higher temperatures tend to produce more crystalline product^[8].

High flow rate tests with the nozzle reactor (Figure 6) showed five distinct mixing patterns, three of which would allow continuous operation, whilst two would probably result in blockages. Inlet Mixing (a) results from the metal salt entering the supercritical water inlet at high flow rates; Down Mixing (e) occurs when the flow rate of the methanol exiting the inner tube is sufficiently high that it

overcomes the inertial forces of the metal salt feed and mixes upstream inside the metal salt inlet. Effective Mixing (b) occurs at a range of flow ratios when the metal salt and supercritical water mix instantaneously at the interface followed by rapid movement up the outer pipe without any separation of fluids; Channelling (c) occurs with high flow rates of the metal salt and specific ratios of the two fluid flows resulting in some fluid partitioning with unmixed metal salt passing up against the

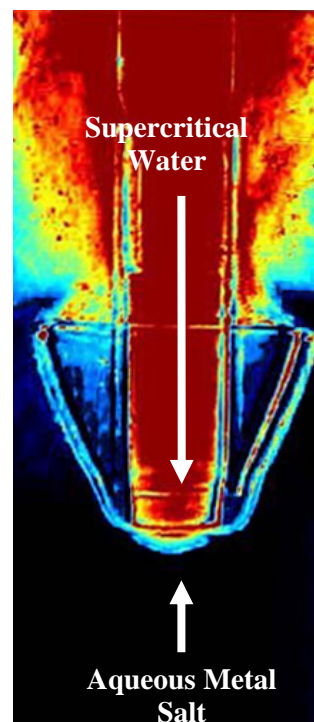


Figure 4 : The Nozzle Reactor

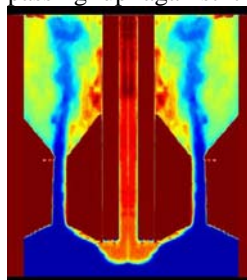


Figure 5 : Shaped interface at the mixing zone of the nozzle reactor

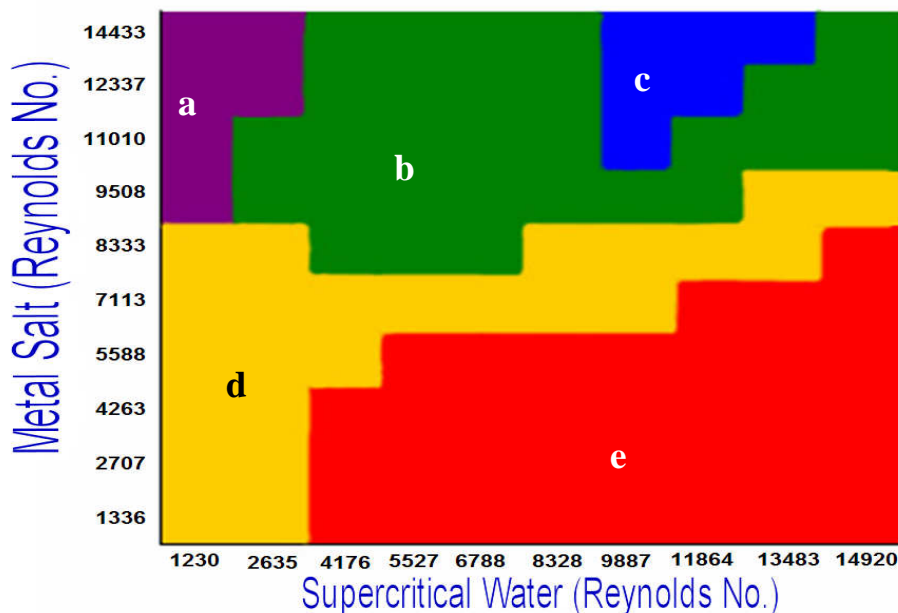


Figure 6 : Flow regimes in the nozzle reactor at high flow rates

outside of the outer pipe; Transitional mixing (d) occurs at a specific ratio of flows to allow the supercritical water mix inside the metal salt inlet, but the mixed fluids then quickly move upstream;

The results clearly show that effective mixing can be achieved at turbulent flow rates but that the flow patterns for each reactor is clearly dependant on the ratio of the two flows as well as their respective flow absolute rate.

4 CONCLUSIONS

Effective mixing of supercritical water with a dissolved metal salt is a significant engineering challenge. Supercritical water has a much lower density than the metal salt and, therefore, has a high degree of buoyancy. Avoiding stagnant zones, back mixing and fluid partitioning is the key requirement of a scWHS reactor. This realisation means that the orientation of the reactor, as well as the relative positions of the inlets and outlets, become key properties in the design of the reactor.

The *Nozzle Reactor* allows the two fluids to mix together in buoyancy induced eddies, without fluid partitioning, stagnant zones forming or back mixing. The rapid mixing downstream increases fluid velocity, reduces residence time and improves particle transportation away from the mixing point. At higher flow rates and flow ratios, the mixing patterns change, but there is scope for optimisation for successful large scale nanoparticle manufacture using the

nozzle reactor. Further work on flow modelling is underway which investigate how the shape of the nozzle interface can be altered to control the mixing patterns downstream.

The nozzle reactor has able to produce over 30 different materials at g/hr scale including silver (30nm), magnetite (10nm), CdS (8nm) and YAG (50nm). Particles can be capped online and transferred directly into a different medium in order to prepare the particles for formulation and/or for controlled increase in particle wt% loading. We are currently scaling up this design and will be able to produce kg/day scale before May 2007.

5 REFERENCES

1. Blood, P.J., et al., Chem. Eng. Sci., 2004. **59**: p. 2853-2861.
2. Adschiri, T., K. Kanazawa, and K. Arai, J. Am. Ceram. Soc., 1992. **75**: p. 1019.
3. Denyer, J.P., *PhD, SChEME*. 2003, University of Nottingham: Nottingham, UK.
4. Clark, W.W., PhD Thesis *SChEME*. 2000, University of Nottingham: Nottingham, UK.
5. Clark, W.W., et al. 2001. New Orleans, USA.
6. Clark, W.W., J.H. Hills, and B.J. Azzopardi. 1998. Newcastle, UK.
7. Clegg, A.J., 1969, University of Surrey: Guilford, UK.
8. Lester, E., et al., ISHR-ICSTR 2006 Symposium Sendai Japan, 2006. **August 5-9th 2006**.