

Investigation of Membrane Emulsification for the Scaled Production of Microcapsules for Self-sealing Cementitious Systems

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Abstract. Capsule-based self-sealing in cementitious systems is an advantageous methodology which has the potential to decrease water ingress and thus enhance a system's durability and extend its lifespan. If capsule-based self-sealing is to be considered as an industrial solution, production must be scaled while capsule quality and batch reproducibility are maintained. In this study, polyurethane-shelled microcapsules containing a commercially available water repellent agent were produced using membrane emulsification equipment, supplied by Micropore Technologies, followed by interfacial polymerisation. Production was scaled across three different cross-flow membrane emulsification devices, the AXF-1, the AXF-3, and the AXF-4, increasing production output to a maximum of 850 L/hr of capsule suspension. Following production, capsules were characterised, measuring average size and size distribution, as well as integrated into a cementitious matrix. The results highlight the key parameters that govern capsule size, the versatility of the equipment, and the consistent quality of capsules produced. It is hoped that this scaled production of capsules will help to develop the commercial viability of capsule-based self-sealing cementitious systems.

1 Introduction

With high loading capacity and durability, cementitious systems have been integral to construction since ancient times. However, crack formation can often cause instability and compromise structural integrity, leading to potential safety hazards and costly repairs or replacement. The use of self-healing materials in cementitious systems, specifically encapsulated materials, promises to extend a structure's lifespan, reduce hazards, and increase sustainability, thus engineering a reduction in waste and helping achieve a more circular economy. [16, 19]

Capsule-based healing offers the unique advantage of delivering targeted healing agents while minimising alterations to the mechanical and chemical characteristics of cementitious systems. [10, 11] The material choice for both the shell and core of the capsules determines the sealing capacity, as well as its effectiveness, durability, cost, and sustainability. [5, 23] Polymers, such as polyurethane, urea formaldehyde, and melamine formaldehyde, have been widely used for rigid, cost-efficient, and effectively triggered shells. [2,18,21]

Despite these advantages, microcapsules have yet to reach an industrial stage, largely because of scaling and cost challenges. [15] It is widely accepted that the cost of additions should not increase the overall cost by more than 20%. The cost of materials, the production methodologies, and the supply chain must reflect this

when formulating any additions. For the construction industry, a large, reasonably priced supply must be consistently available to ensure that to-scale additions can be achieved. [6, 11]

Another key challenge is the reliability and consistency of the product and how it is incorporated into cementitious systems. When novel manufacturing techniques are employed, such as microfluidics, product consistency is preserved, with the coefficient of variation often in the single digits. However, although progress has been made in recent years, microfluidics does not yet match achievable production output when compared to industrial staples such as colloidal mills or high-shear homogenisers. [17] There is a significant gap between increased production output and the consistency of the product.

One possible production solution is membrane emulsification (ME), a scalable emulsion formation technology that exhibits minimal product variability, depending on the formulation used. [8, 9] Since the mid-'90s, reliance on membrane emulsification has sharply increased both in academic research and industry. [12] Since then, there has been a further expansion of membrane materials, pore size, pore layout, and operating principles. [14, 22]

ME offers manufacturing advantages by improving mechanical stability, narrowing capsule size distribution, allowing a scalable and continuous process, and decreasing energy and material consumption. [22] Because of these characteristics, ME has become a

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staple process in agriculture (encapsulating fertilisers), pharmaceuticals (drug delivery), health care (encapsulating actives), and food (flavour enhancement). In this study, the use of ME in the scaled production of microcapsules for self-sealing cementitious systems was investigated. This study used stainless steel membranes with laser drilled pores in Advanced Cross Flow (AXF) equipment, all provided by Micropore Technologies. A schematic can be seen below in Figure 1.

The AXF uses a continuous phase flow as the shear needed for droplet detachment. The continuous phase is pumped through the length of the inner section of the tubular membrane. The dispersed phase fills the space surrounding the outside of the membrane before being pressurised through the membrane. Droplet growth occurs at the inner surface of the membrane and detach from the shear force generated by the continuous phase flow.

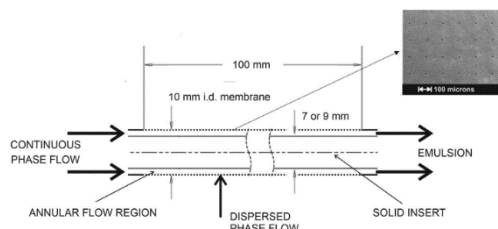


Fig. 1. Schematic of AXF Membrane Emulsification (modified from Holdich et al. with permission)

As mentioned, one of the challenges of integrating self-sealing capsules into industrial processes is developing reliable scaling techniques. [12] In this study, scaled production using membrane emulsification was investigated in two ways: extended production runs on a single membrane and production runs on Micropore's AXF-N, a scaled-up piece of equipment. The AXF-N operates in the same manner as the AXF-1. However, parallel units are manifolded together to increase production output. The number of parallel units linked is user-dependent. For this study, three (AXF-3) and four (AXF-4) parallel units were trialled. Figure 2, below, depicts the AXF-7 and the AXF-1.

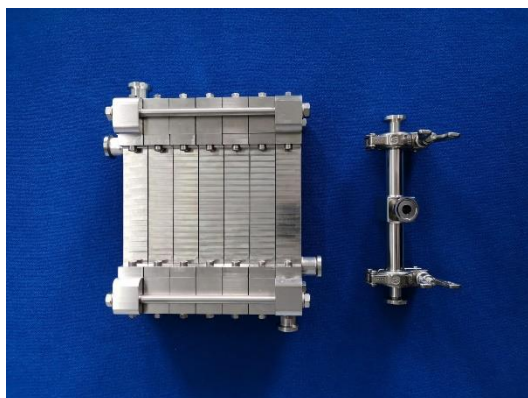


Fig. 2. The AXF-7 (L) Next to the AXF-1 (R)

As described in the literature, membrane characteristics, phase parameters, and operating parameters affected the emulsion formed, its stability, and, consequently, the end capsule product. In this study, production trends were studied on the AXF-1,

AXF-3, and AXF-4 as operating and phase parameters were varied. The respective trends were then compared to better understand how emulsions and capsules could be scaled-up for cementitious systems.

2 Materials and Methods

2.1 Materials for Emulsions

Oil-in-water emulsions were formed using light density mineral oil, supplied by Merck & Co., and an aqueous polyvinyl alcohol solution formed using deionised water and polyvinyl alcohol grade 23-88, supplied by Fisher Scientific. All chemicals were used without further purification.

2.2 Materials for Capsules

Capsules were formed from an oil-in-water emulsion followed by polyurethane shell formation via interfacial polymerisation. The oil phase of the emulsion was a well-dispersed mixture of Sikagard-705L, a one-component, solvent free, low viscosity alkoxy silane water repellent agent (WRA) supplied by Rawlins Paints, and a diisocyanate, isophorone diisocyanate (IPDI), supplied by Fisher Scientific. Sikagard-705L, the core material, is commonly used in the construction industry as a water-proofing sealant, hydrophobising surfaces through a process called silanization. Silanization occurs at the cementitious surface as hydroxyl groups replace the alkoxy groups found in the WRA, forming covalent bonds between the silane and the minerals in cementitious surface. The aqueous phase was a polyvinyl alcohol solution formed using deionised water and polyvinyl alcohol grade 23-88, supplied by Fisher Scientific. Shell formation was synthesised using a diol-source, 1,4-butanediol supplied by Fisher Scientific, added to the aqueous phase post-emulsion formation. A catalyst was added, dibutyltin dilaurate (DBTDL), supplied by Fisher Scientific. All chemicals were used without further purification.

2.3 Emulsion Formation using ME

Three pieces of Micropore's AXF equipment were used to produce emulsions and/or capsules: the AXF-1, the AXF-3, and the AXF-4. Each stainless steel membrane had pores with a diameter of 10 μm . The same membranes were used for all runs. Membranes were cleaned pre- and post-use according to a standard procedure specified by the supplier to ensure adequate wetting, and thus the hydrophilicity, of the membrane surface.

Fluids were pumped in both continuous and dispersed phases with Ismatec MCP-Z Gear Pumps, supplied by Cole-Parmer. The pumps were calibrated prior to each run to ensure that the collected volume was correct. The flow rates of the continuous and dispersed phase flows varied, depending on the run. However, the flow regime was always laminar, as calculated by the Reynolds number. This prevented excess shear causing droplet breakup and polydisperse product.

It is important to note that, for the AXF-3 and AXF-4, where the flow rates were tripled or quadrupled, respectively, the flow rate across an individual membrane remained laminar. This is because the pressure drop into each parallel block was greater than that of the flow across the manifold. This helped to ensure that there was an even flow distribution across each of the parallel blocks.

Emulsions were also produced using a high-shear homogeniser (IKA T18 digital Ultra Turrax) as a means of comparison. The rpm was 3000, 5000, or 7000 while emulsification took place for 30 seconds. In all cases, the emulsion percentage was ten.

2.4 Capsule Shell Formation

The polyurethane shells of the capsules were synthesised from isophorone diisocyanate and 1,4-butanediol via interfacial polymerisation. Following emulsion formation using ME, the product was collected into a reaction vessel where shell synthesis took place. The product was continuously stirred using an overhead stirrer at 200 rpm. The reaction vessel was heated to 63 °C using a heating coil connected to a water-heated Julabo 200F. 1,4-butanediol acted as the diol source for polyurethane formation and was added dropwise in a 1:1 ratio for NCO:OH. A 100 µL addition of the catalyst DBTDL was then added. The reaction was carried out for two hours to ensure completion.

2.5 Emulsion and Capsule Characterisation

The diameter of the droplets and capsules, as well as the size distribution of a representative sample, was measured using a Jorin Visual Process Analysis (ViPA). More than 10,000 measurements were taken with a dilute sample, and data was analysed to ensure correct differentiation between bubbles and the droplets and capsules. Visual analysis was performed using a Meiji GXCAM-U3-5 optical microscope.

Capsules were integrated into cement paste to visualise the distribution of capsules. The cement paste was made with a water-to-cement ratio of 0.4 (tap water) and ordinary Portland cement (CEM I 52.5N, Blue Circle Industries). Microcapsules were added at 3% by weight of cement (bwoc) in a slurry format stirred into the mixing water. Water and cement were added to a mixing container at the same time and, using a hand mixer, mixed for one minute, allowed to stand for 30 seconds, and mixed for an additional minute. The fresh paste was casted in prismatic moulds (20 x 20 x 35 mm³) covered in mineral oil. Once cast, prisms were covered in plastic film and stored in laboratory conditions (20 ± 2 °C). The following day they were demoulded and wrapped again in plastic film and stored in laboratory conditions (20 ± 2 °C) until day 7.

Scanning electron microscopy (SEM) using a Nova nanoSEM 450 under an 8 kV accelerating voltage was used to study the integration of the microcapsules into a cement matrix. Samples were dried at room temperature and mounted on aluminium stubs. Prior to SEM imaging, samples were gold sputtered.

3 Results

3.1 Emulsion Production on the AXF-1

The emulsions created using the AXF-1 at varied operating or phase parameters demonstrated baseline trends before producing capsules or producing capsules at scaled volumes. As seen in Figures 3 and 4, there is a linear trend between increasing continuous phase flow rate (consequently, shear felt at the membrane surface) and decreasing D50. This aligns with the literature, as the increasing shear affected the force balance on the forming droplet, decreasing the amount of droplet growth time. The trend lines of the D10, D50, and D90 have similar slopes, -0.044, -0.046, and -0.036, respectively, showing consistency in droplet distribution as shear varied. For the emulsions depicted in Figure 3, all CV values were below 20% and half below 15%, demonstrating a monodisperse product. However, at increased shear there was a slight widening of the distribution curve. This demonstrates that increased membrane shear can cause premature detachment of smaller droplets and a left skewed distribution.

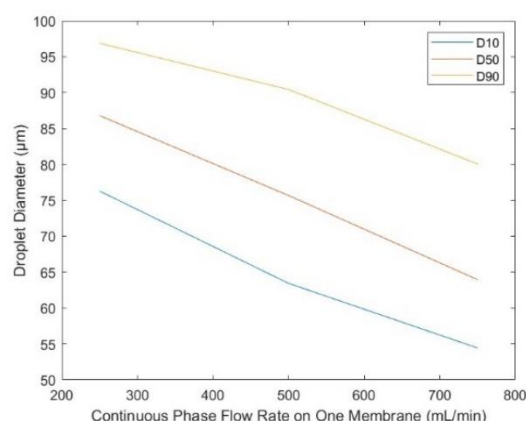


Fig. 3. Effect of Continuous Phase Flow Rate on Droplet Size Distribution Using the AXF-1 (all at a 10% Emulsion)

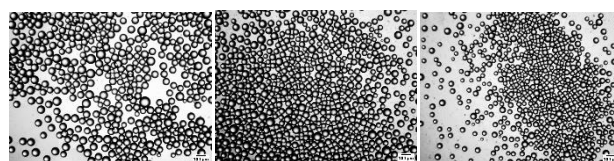


Fig. 4. OM Images of Emulsions Produced at Increasing Continuous Phase Flow Rates Using the AXF-1 (L) 250 mL/min (C) 500 mL/min (R) 750 mL/min

The use of stabilisers in emulsion formation is essential because they modify the interfacial tension at the liquid-liquid interface. In addition, stabilisers entrap droplets with larger polymeric molecules, allowing further control of the achieved droplet size and size distribution. The direct effect of this can be seen in Figure 5, as a decreased concentration of stabiliser in the continuous phase increased the D50 for both emulsion and capsules. Decreased stabiliser can also have a widening effect on droplet distribution because of decreased entrapment. Thus, although modification of stabiliser grade, pore size, and formulation densities can be altered to produce the optimal size with a

monodisperse distribution, the consequences (i.e., increased span) must also be considered.

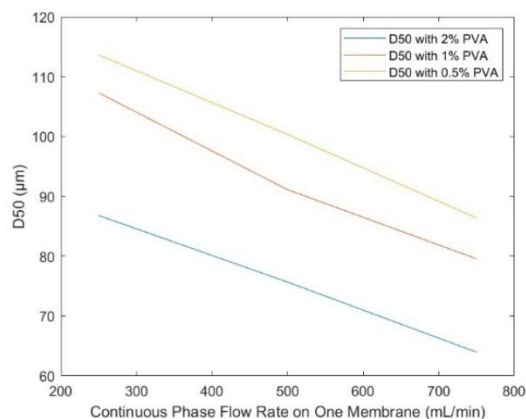


Fig. 5. Effect of Stabiliser Concentration on Droplet D50 Using the AXF-1 (all at 10% Emulsion)

3.2 Capsule Production on the AXF-1

With capsule production on the AXF-1, it was demonstrated that, although alterations in formulation affected the D50 achieved from a specific shear, the same trend is apparent. This increased production control, allowing capsule size to be easily altered. Optical microscopy (Figure 6) confirmed wall formation after the polyurethane reaction, with a smooth surface with slight dimpling because of the reaction.

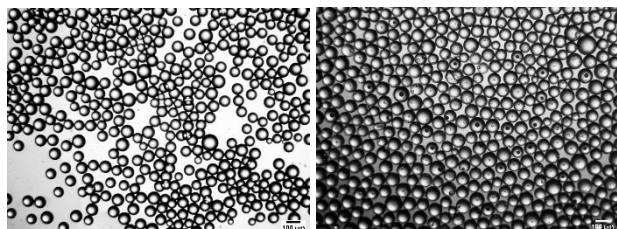


Fig. 6. OM Images of Droplets (L) and Capsules (R) Produced Using the AXF-1 at the Same Operating Parameters

Capsules were integrated into cement paste and the prisms cracked to better view the capsule-to-cementitious bond (Figure 7). It was seen for capsules of both larger and smaller sizes that there was successful integration and successful mechanical triggering upon manual cracking of the specimen. Not all capsules, however, ruptured at the crack face, which can be explained by variation in shell thickness and in rupture force during cracking. This might prove beneficial under cyclic cracking and sealing.

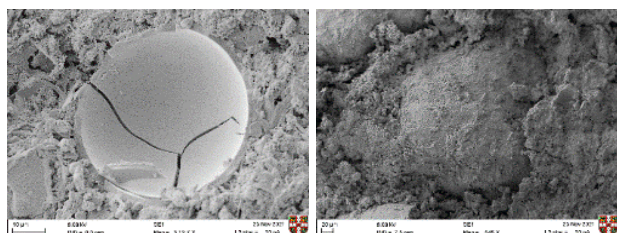


Fig. 7. (L) Triggered Microcapsule (R) Untriggered Capsule in Cement Paste

3.3 Scaled Production of Capsules

Because the AXF-1 operates continuously, by increasing the length of the production run an ever-increasing volume of product can be outputted, depending on feed vessels and reaction tanks. Here, the emulsion production run lasted for one hour (shell synthesis occurred for an additional two hours), with a throughput of 30 L of product, which translated to 3L of dry capsule weight. Samples were taken throughout the run to investigate changes in droplet D50 and size distribution. In the table below, it can be seen that there was no visible trend of capsule size or size distribution and time; the D50 varied only $\pm 2 \mu\text{m}$ throughout the entirety of the run. This demonstrates the robustness of the formulation and the utility of the equipment. It also demonstrates that there were minimal membrane blockages during production. If a blockage of pores had occurred, the dispersed phase flux would have increased, causing a widening of the size distribution.

Table 1. Effect of Time on D50 and CV of Capsules Produced Using the AXF-1

Time	15 min	30 min	1 hour
D50 (µm)	89.13	88.28	88.36
CV (%)	16.30	15.36	16.58

3.4 Scaled Production of Emulsions

Scaled production of emulsions was also investigated using the AXF-3 and AXF-4. When using this equipment, the continuous phase and dispersed phase flow rates investigated on the AXF-1 were tripled or quadrupled, respectively, to ensure the same shear at each membrane surface and to ensure that the dispersed phase flux was preserved. As with the AXF-1, a clear linear trend between the D10, D50, and D90 and the continuous phase flow rates was seen for both the AXF-3 (Figure 8) and the AXF-4 (Figure 9). However, the slopes of the lines vary more than those of the trend lines for AXF-1 production.

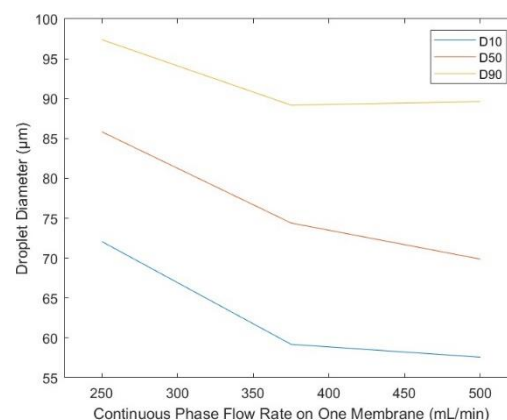


Fig. 8. Effect of Continuous Phase Flow Rate on Droplet D50 Using the AXF-3

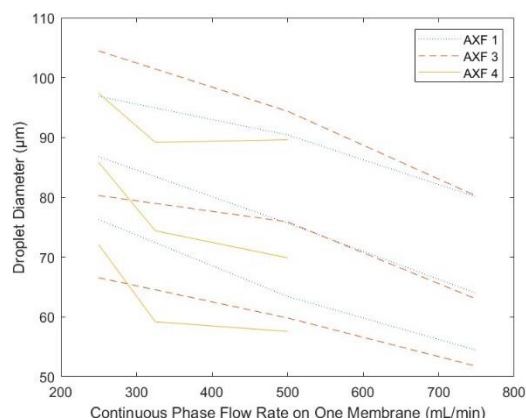


Fig. 9. Effect of Continuous Phase Flow Rate on Droplet D50 Comparing the AXF Equipment

Theoretically, there should be minimal variation of the achieved D50s on the AXF-1, AXF-3, and AXF-4 when producing capsules at the same flow rate with each membrane. However, the minimal variation that was seen could have been caused by variability in the porosity of the membranes. The effect of any variation in pore diameter or pore shape on each membrane was tripled or quadrupled with the AXF-3 and AXF-4, respectively, leading to a widening of the droplet distribution, especially when the dispersed phase flux was high. It is also important to note that droplet formation was influenced by phase parameter changes. Because the experiments were not performed in a temperature-controlled environment, minor viscosity changes could have altered achieved D50s and size distributions.

Emulsions were also produced on a homogeniser as a means of comparing scaled results to a widely used technology in an industrial setting. In Figure 10, there is no prominent trend between D50 and the shear applied. High pressure homogenisation is a less controlled method of droplet formation, often requiring multiple passes to achieve the size required, while still exhibiting wider CVs and greater variability. This is depicted in Figure 11, where the droplet size distribution of emulsion formed used a homogeniser and an AXF-1 are compared. If membrane emulsification can produce the volumes required for industrial scale applications (either in longer continuous production runs or through manifolded blocks), the achievable size distributions would become much narrower.

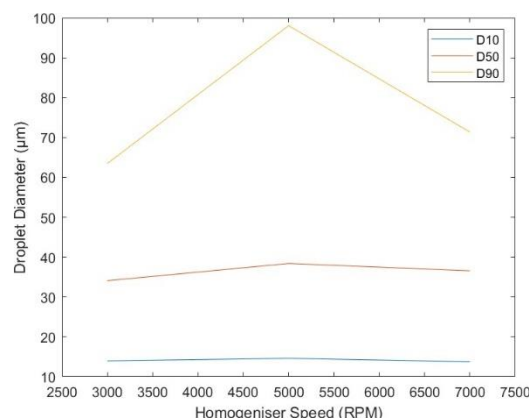


Fig. 10. Effect of High-Shear Mixing Using a Homogeniser on Droplet D50

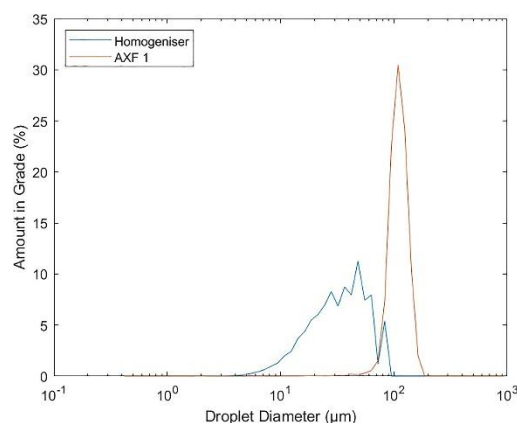


Fig. 11. Comparison of Droplet Size Distribution When Using the AXF-1 or a High-speed Homogeniser

Production trends of the AXF-1 and AXF-3 were also compared when varying stabiliser concentrations. As seen on the AXF-1, as the stabilised concentration decreased, the droplet D50 increased on the AXF-3 (Figure 12). There was variation between the AXF-1 and AXF-3 for the same reasons as above, i.e., possible variations in the membranes and the temperature.

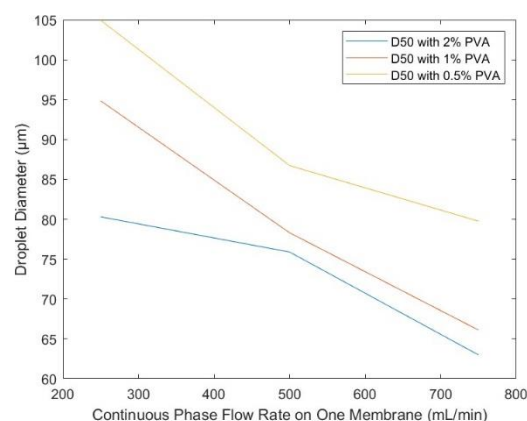


Fig. 12. Effect of Stabiliser Concentration on Droplet D50 Using the AXF-3 (all at 10% Emulsion)

3.5 Product Reproducibility

When production is scaled, ensuring batch reproducibility becomes crucial to reduce material, energy, and production time waste. For all three pieces of ME equipment, reproducibility was assessed. Variation was minimised by ensuring that the same membranes and equipment sets, the same batch of material, and the same measuring equipment were used. However, some runs were performed on different days, meaning that some environmental fluctuations, such as temperature, must be considered. In table 2, the droplet D50s of the repeatability studies are listed and, in Figure 13, the droplet size trend lines are compared for repeat AXF-1 runs. Again, it was found that there was more variation when comparing the results of the AXF-3 and AXF-4 to the AXF-1 because variation is multiplied through the manifolded blocks and possible pore variation in the membranes.

Table 2. Investigating Repeatability on the AXF Equipment Using Droplet D50 with a Continuous Phase Flow Rate of 500 mL/min at 10% Emulsion

Equipment	Run A (µm)	Run B (µm)	Run C (µm)
AXF-1	77.82	75.66	75.90
AXF-3	75.89	70.89	76.03
AXF-4	74.04	75.87	72.38

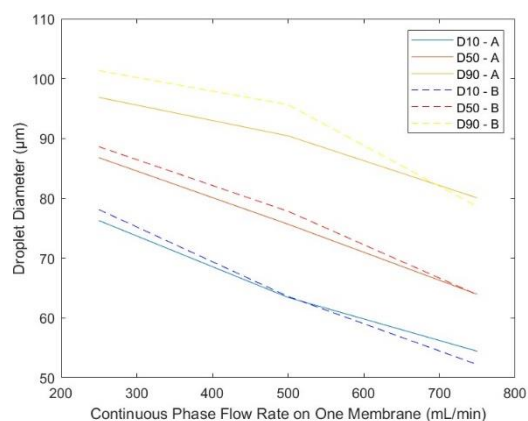


Fig. 13. Investigating Repeatability on the AXF-1 Using Droplet D50

4 Discussion and Conclusions

In this study, membrane emulsification was used to produce emulsions and capsules at scaled volumes in order to meet the demands of the cement and construction industries. Three different pieces of membrane emulsification equipment were used: the AXF-1, the AXF-3, and the AXF-4, all producing droplets via the shear generated from the continuous phase flow through the membrane. Three different continuous phase flow rates, three dispersed phase flow rates, and three PVA concentrations in the continuous phase were tested. In addition, their individual and combined effects on droplet size and distribution were further investigated. By understanding their combined effects, formulation specific models can guide the user, allowing enhanced control when optimising droplet size and distribution. It is essential to understand how to vary

the properties of an emulsion when specific parameters need to be constant.

As production volume scaled, a deeper understanding developed of how the equipment used affected the emulsion formed and, consequently, the capsules produced. It was seen that as production scaled from the AXF-1 to the AXF-4, there was a gradual widening of the size distribution and some variation in the achieved D50s, despite keeping all parameters and materials constant. As the size of the capsule affects the core content and the shell thickness, minimal variation in D50 will lead to a more consistently triggering product. This consistency might be achieved through the choice of membrane, a formulation specific surface response model, or through in-line control that allows real time alteration to key parameters. However, when comparing scaled AXF performance to that of high shear homogenisation, the industry standard, membrane emulsification offers advantages, such as enhanced repeatability and user-led and trend-depicted control of each piece of the investigated AXF equipment. Because this would be used in construction applications, regulations regarding size distribution are not so stringent as when producing microcapsules for pharmaceutical or food products. However, as self-healing and self-sealing cementitious systems progress, greater control of capsule distribution, and the ability to tighten and widen distribution via parameter controls, will be essential to ensure optimal triggering and the enhancement of structural integrity.

This investigation expanded upon the current body of literature, which has shown membrane emulsification to be an effective advanced technique for batch and continuous lab scale production. The positive results demonstrate that emulsions and capsules produced using membrane emulsification are controllable, repeatable, and scalable. One suggestion for further work would be to focus on expanding the data for this formulation to a full surface response model, thus broadening and deepening our understanding of how the equipment used can continue to advance scaled capsule production. As this study demonstrates, at least some solutions to our global social, economic, and environmental problems can be found at the macro level.

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