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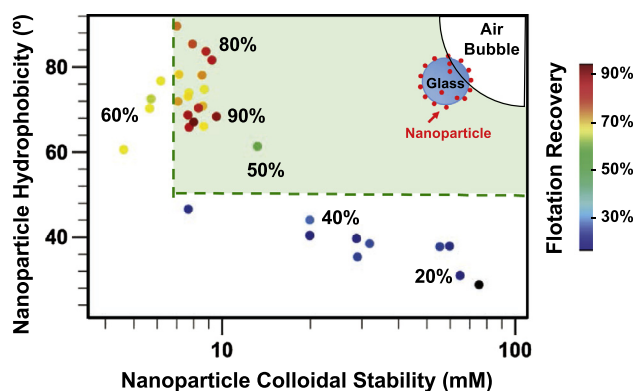
Choosing mineral flotation collectors from large nanoparticle libraries

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GRAPHICAL ABSTRACT



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ABSTRACT

Polystyrene nanoparticles can promote froth flotation of mineral particles if the nanoparticles are sufficiently hydrophobic and are colloidally stable in the high ionic strength solutions typical of commercial flotation operations. A library of 80 unique polystyrene nanoparticle types was prepared with click chemistry and used to determine if particles that were sufficiently hydrophilic to be colloidally stable in high ionic strength and high pH solutions, were also capable of promoting flotation. The conflicting requirements of colloidal stability and hydrophobicity can be achieved in 9 mM sodium carbonate, a very challenging environment. Instead of testing all 80 samples with laborious flotation testing, automated assays measuring colloid stability and nanoparticle hydrophobicity were employed. The colloid stability assay measured the critical coagulation concentrations (CCC). Nanoparticle hydrophobicity was characterized by water contact angle, measurements (CA). A smaller cohort of the most promising nanoparticle candidates for detailed flotation testing were identified by mapping nanoparticle properties on the CA versus CCC plain – a “Flotation Domain Diagram”. We believe that this work was the first time that combinatorial synthesis and high throughput screening have been used in the development of flotation chemicals. Finally, based on the accumulated evidence, effective nanoparticle flotation collectors are likely to be ~ 50 nm in diameter, with a soft hydrophobic polymer shell and with surface functional group densities in the order of magnitude of 0.1 nm^{-2} .

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1. Introduction

Froth flotation is one of the most important separation operations in mineral processing [1]. Typically ore is ground to give an aqueous suspension of large ($\sim 100 \mu\text{m}$ diameter) particles that

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are mainly unwanted “gangue” minerals mixed with a small quantity of the desired mineral particles. The mixed suspension is treated with a hydrophobic surfactant, called a collector, which selectively adsorbs on the valuable particles, rendering them more hydrophobic. The treated mineral particles adhere to air bubbles in the flotation cell, concentrating the mineral in the froth at the top of the flotation cell.

We have been developing nanoparticle flotation collectors to replace molecular-scale conventional surfactant-based technologies. The larger nanoparticles may offer advantages when treating mineral surfaces contaminated with nanoscale debris [2]. Following the pioneering work out of the University of British Columbia [3–5], we have focused on polymeric latex nanoparticles as potential flotation collectors. We briefly evaluated inorganic nanoparticles with limited success [6]. However, other groups have recently demonstrated promising inorganic nanoparticle flotation collectors [7,8].

Our initial development work involved small scale laboratory batch flotation tests, either with a real mineral ore or with glass beads, a cleaner system for mechanistic studies. The main observations from our early work were: (1) adsorbed, surfactant-free polystyrene latex was sufficiently hydrophobic to promote mineral or glass bead flotation [9]; (2) 50 nm diameter nanoparticles were far superior flotation collectors compared with larger particles or aggregates [10]; and, (3) soft nanoparticles [11] or nanoparticles with a soft shells [12] were superior to polystyrene because deformable particles were more strongly adhering to mineral surfaces. As our development work progressed from glass beads in low ionic strength media to commercial ground ores, it became apparent that nanoparticle aggregation in the high ionic strength flotation media was a significant problem [13]. Note that aggregation is not an issue with traditional water soluble, single molecule collectors such as potassium amyl xanthate.

Potent nanoparticle flotation collectors must have surface chemistries that satisfy three key requirements: (1) the nanoparticles must be sufficiently hydrophobic so that mineral particles decorated with adsorbed nanoparticles will attach to air bubbles; (2) the nanoparticles must be colloidal stable in the ionic strength conditions of the flotation cell; and, (3) the nanoparticles must not specifically deposit onto the desired mineral particles and not on the gangue particles. These requirements are a challenge because surface chemical species, such as charged groups or hydrophilic oligomers that improve nanoparticle colloidal stability, also lower the nanoparticle surface hydrophobicity.

Nanoparticle Surface Property Space

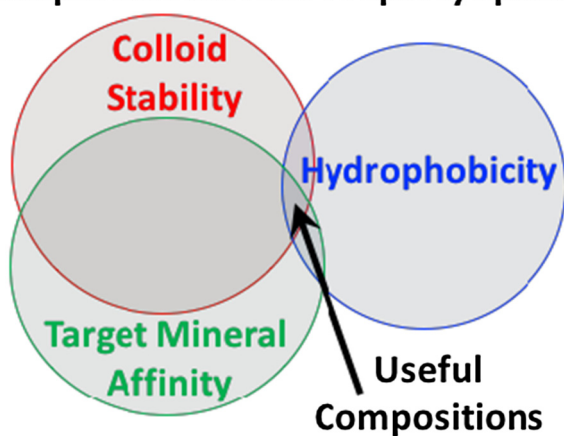


Fig. 1. Nanoparticle surface chemistry property space illustrating the conflicting requirements of hydrophobicity, colloidal stability, and specific affinity to mineral surfaces.

The nanoparticle design challenge is illustrated by the Venn diagram in Fig. 1. We propose that the mineral affinity circle nearly overlaps the colloid stability circle because mineral affinity functional groups, such as amines, imidazoles, chelating agents, and xanthates, can also contribute to colloid stability. As drawn, the Venn diagram includes an overlap region where the three circles overlap, indicating a set of surface compositions where nanoparticles should be effective collectors. The goal of our work was to prove that it possible to generate nanoparticle surface compositions that exist in the “Useful Compositions” domain of the Venn diagram in Fig. 1. A secondary goal was to demonstrate a high throughput strategy for designing nanoparticle flotation collectors. As a first step, herein we focus on two of the properties – colloid stability and hydrophobicity. These are a generic requirement for all mineral flotation operations, whereas mineral affinity is specific to the mineral type.

Our early development efforts involved preparing nanoparticle candidates by emulsion polymerization, cleaning the particles, characterizing the particles and measuring their flotation characteristics. This was a labor-intensive approach that was not appropriate for probing the very large variable space of nanoparticle surface chemistries. In these early studies, we introduced the concept of the “Flotation Domain Diagram” in which candidate nanoparticle properties are mapped onto a 2-dimensional surface. One axis of the surface is the critical coagulation concentration (CCC), a measure of the colloidal stability, and the other axis is the water contact angle (CA) on a glass surface saturated with adsorbed nanoparticles, a measure of hydrophobicity [14]. Fig. 2 illustrates the Flotation Domain concept; nanoparticles with properties falling within the green zone are candidates for flotation testing, whereas particles outside the domain are too colloidal unstable or are too hydrophilic. The contact angle boundary for flotation was fixed to 50° based on experimental observation [9], whereas the CCC boundary is determined by the operational conditions in the target commercial flotation cells.

Herein, we describe a high throughput screening (HTS) approach for identifying the most promising candidate nanoparticle types from large libraries of unique nanoparticle types. HTS has two requirements: (1) a library of candidate particles spanning a large range of nanoparticle properties, and, (2) automated, simple, small scale screening tests that reject non-promising candidates.

In this work, we used click chemistry [15,16] to generate a combinatorial library of 80 unique nanoparticle types. Our synthetic approach involved fluid handling robots and is easily scalable to

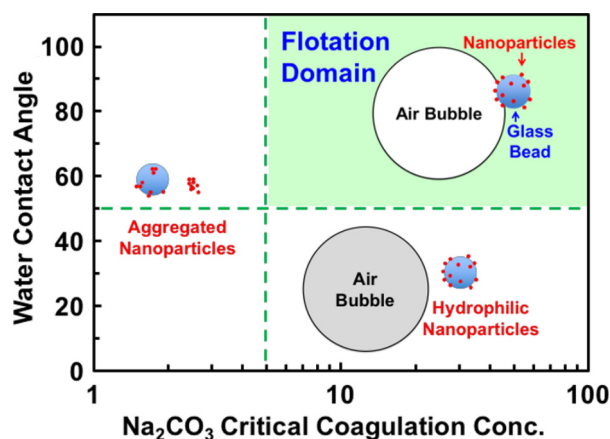


Fig. 2. Illustrating the Flotation Domain analysis where nanoparticle properties are mapped onto the CA versus CCC plain. The CCC > 5 mM criterion for flotation was based upon solution properties in a commercial flotation cell whereas the CA > 50° criterion was based upon experimental results [9].

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