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# MICRO-FLOATABILITY OF RUTILE AND ZIRCON WITH SOAP AND AMINE TYPE COLLECTORS

Single-mineral floatability of pure, heavy sand rutile and zircon minerals using sodium oleate and hydrogenated tallow amine acetate as collectors was studied by a micro-flotation device over a wide pH range from 2 to 12, at three levels of the collectors and two levels of a polypropylene glycol type frother. Rutile yielded a peak foatability at pH 6 with sodium oleate, and floated reasonably well over a wide pH range from 2 to 8 with the amine collector. An abrupt deterioration of the floatability of rutile was observed at pH>8. The maximal floatability range for zircon was from pH 6 to 10, followed by a sharp decrease at pH>10, with both of the collectors. The floatability of zircon decreased sharply with decreasing pH in the acidic medium, below pH 6. The results were discussed in view of collector species distribution as a function of pH to suggest adsorption mechanisms for the collectors. The upper critical flotation pH values for the minerals seemed to be sufficiently distinct to suggest a potential for the differential flotation of the minerals in the alkaline medium with both of the collectors tested.

## INTRODUCTION

Rutile ($TiO_2$) and zircon ($ZrO_2.SiO_2$) are among the valuable constituents of heavy mineral sand deposits and contribute heavily to the economic viability of a majority of existing plant operations. Natural rutile is the favored feedstock mineral for the production of white $TiO_2$ pigment through the chloride process (Stanaway, 1994), and mainly used in the coatings, plastics and paper industries (Pearson, 1999). Zircon is sourced as a by-product of titanium minerals production from heavy mineral sand deposits. The most important market for zircon is as an opacifier for ceramic tiles and sanitarywares in the form of zircon flour (micronized to 100% finer than 6μm). The other major applications for zircon are as a ground product in the manufacture of frit (micronized to 95% finer than 45μm), as a component of refractories, particularly in glass furnaces, and as a moulding sand in the foundry industry (Pearson, 1999).

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Conventional rutile and zircon sand production begins with dredge mining of heavy mineral deposits, followed by gravity concentration, mostly through the use of Humphrey's spirals. The gravity concentrate is then dried and subjected to a series of magnetic and high-tension separations for commercial production of titanium minerals (rutile, ilmenite) and staurolite (or garnet) sands. The tailing from the dry process, enriched in zircon and silica sand, undergoes a wet upgrading by spirals and shaking tables to reject the silica sand and other $Al_2O_3$-containing minerals such as kyanite and sillimanite. The zircon gravity concentrate, typically containing 95% zircon, is then dried (or calcined at 500-700°C) for subsequent upgrading by dry separation equipment such as high-tension rolls, induced roll magnets, and electrostatic plate separators to produce a concentrate having a grade of +97% $ZrO_2.SiO_2$.

The conventional processing methods work efficiently for particles coarser than 75μm. Significant loss of productivity occurs in finer sizes, and the separation process becomes uneconomical below 45μm particle size. Commercial rutile and zircon concentrates have tight specifications for the inclusion of the other mineral. In many applications, the $TiO_2$ content in zircon concentrate should not be higher than 2%. Likewise, for premium-quality zircon the $TiO_2$ content is limited to no more than 0.2%. Such levels of purity cannot be obtained even with the advanced fine-particle gravity separation at sizes below 45μm. The froth flotation process remains as a sensible research alternative for the selective separation of zircon from titanium-bearing minerals (rutile and ilmenite), contained in the fine-sized tailings of conventional mineral sands treatment operations.

There exist a limited number of studies reported in the literature with regard to flotation characteristics of zircon and rutile. Flotability of pure zircon and rutile minerals with sodium oleate as collector was studied by Madhavan et al. (1965) as a function of pH. They found that the lower critical pH value for the flotation of zircon was 1.5 and that of rutile 2.6, which indicated the possibility of separation of zircon and rutile in the acidic medium. The upper critical pH values were so close (10.5 and 10.6, respectively) that differential flotation of the two minerals did not seem to be possible in the alkaline medium. They also reported that zircon, when once coated with sodium oleate, did not desorb either at higher or lower pH, whereas sodium oleate seemed to be a desorbing collector from the rutile surface either below the lower critical pH or above the higher critical pH. Plaksin et al. (1967) reported similar findings for the flotation of zircon with sodium oleate alone, indicating its ready flotation in neutral, slightly acidic, and slightly alkaline media. They did not find any significant adverse effect of a triatomic phenol depressant (pyrogallol) on zircon flotability. Sodium sulhide and caustic soda were found to desorb sodium oleate from zircon surface (Pol'kin et al., 1967). Li and Box (1995) examined selective flotation of zircon and rutile under hot soap (sodium oleate) conditions, and achieved high zircon recoveries (97-98%) in the 8.5 to 11.2 pH range, at a conditioning temperature of 90°C, giving the lowest $TiO_2$ grade (2.4%). Paves and Peres (1993) reported that a

commercial hydroxamate collector could readily float both zircon and rutile in the wide pH ranges 2.5 to 9 and 3 to 8, respectively, while sodium metasilicate was reported to effectively depress both minerals. Modified phosphoric acid ester and styryl phosphonic acid collectors were also tested for the flotation of rutile in slightly acidic media from some hard-rock rutile ores (Bulatovic and Wyslouzıl, 1999; Liu and Peng, 1999).

Probably the first major commercial flotation of zircon from heavy mineral sands has been considered for Sierra-Leone Operations with the intention of the separation of zircon from rutile at sizes finer than 100 mesh. In one proposed scheme, zircon was floated using a cationic amine collector at pH 2.5. Sodium flouride was used to activate the zircon, and starch was used to depress the titanium oxides. In an alternative scheme, quartz was floated with amine at pH 10 while the titanium oxides were again depressed by starch. The pH was then lowered to 2.5 and amine was used to float the zircon after activation with sodium fluoride (Davies et al., 1994).

It is apparent from the literature that there exists a need for an efficient industrial flotation scheme for separation of fine-grained zircon from titanium-bearing minerals in order to reprocess accumulated tailings of conventional dry processes and/or to devise new processing schemes to replace the conventinal methods so as to improve overall recovery. This need calls for a fundamental understanding of the flotation properties and surface characteristics of zircon and titanium-bearing minerals (mainly rutile and ilmenite), as well as those of some other mineral constituents associated with these minerals, in the light of recent advances in froth flotation science.

As a part of ongoing extensive research on the flotation behavior of zircon, rutile, and ilmenite, this paper presents some initial findings with regard to single-mineral micro-flotability of zircon and rutile in the presence of sodium oleate or hydrogenated tallow amine acetate, over a wide pH range from 2 to 12.

## MATERIALS AND EXPERIMENTAL METHODS

### MİNERAL SAMPLES

The zircon mineral sample used in this reseach was obtained from DuPont's Starke, Florida Operations. Already calcined at about 550°C in a rotary kiln partly for improving its appearance (color), the sample was designated as Premium Zircon Sand, and contained 67.22% $ZrO_2$, 31.11% $SiO_2$, and 0.11% $TiO_2$.

The rutile mineral sample was also obtained from DuPont. As-received sample was further purified by a high-intensity, dry magnetic separator (Permroll) so as to remove iron-bearing impurities. The purified sample, after repeated washing with distilled water, assayed 96.66% $TiO_2$, 0.48% $SiO_2$, 0.39% $ZrO_2$, and 0.32% $Fe_2O_3$.

Both mineral samples were wet screened with distilled water to yield 150x200 mesh (106x75 μm) size fractions for micro-flotation tests. These sized test samples were pretreated with 10% HCl solution, and then washed repeatedly with distilled

water to clean the mineral surfaces, and dried at 60°C for use in the micro-flotation tests.

Zeta-potential measurements with the same samples in our earlier studies revealed that the iso-electric points of the rutile and zircon occured at pH 3.5 and 4.4, respectively (Köse et al., 2000; Muratoğlu et al., 2000).

## REAGENTS

Sodium oleate (Na-Ol), manufactered in our laboratory, and a commercial (Akzo Nobel) sample of hydrogenated tallow amine acetate, HTAA ($RNH_3Ac$, where R is 96% $C_{18}$), were used as collectors. A stock solution of 0.1M total oleate concentration was prepared by neutralization of analytical-grade oleic acid with NaOH in distilled water. For preparing the amine stock solution, 0.1g solid prills (MW: 331g) of the amine collector was dissolved in distilled water in a 250-ml volumetric flask that was placed in a water bath maintained at 70°C. A desired concentration of collector solutions were freshly prepared by subsequent dilutions from the stock solutions.

Dilute solutions of HCl and NaOH were used as pH regulators. The polypropylene glycol type frother Dowfroth 400 was used as a frother at two concentrations, 50 ppm and 100 ppm.

## MİCRO-FLOTATİON TESTS

The microflotation tests were performed in an automated shaking test-tube instrument, the EMDEE Microflot Agitator (Chudacek, 1991). A sample mass of 0.4g was conditioned in 70ml of the test solution in a centrifuge test-tube for a required time, using gentle magnetic stirrer agitation. The stirrer bar was then removed, the tube was stoppered and vigorously agitated in the Microflot agitator for 20 cycles. During agitation a mineralized froth was formed, which was then removed using a pipette. The froth fraction was dried overnight, and weighed to yield flotation recovery in the single-mineral floation system of this study.

In the conditioning stage, the mineral test sample was first stirred in distilled water for 5 minutes, and then the pulp pH was adjusted by the addition of HCl or NaOH solutions. A predetermined amount of collector solution was added into the pulp to obtain the desired concentration, and the pulp was further conditioned for five minutes. Then, the frother solution was introduced into the gently stirred pulp in the test tube, and the tube was immediately placed in the agitator. Each test was repeated twice. All tests were carried out at room temperature.

Micro-flotation tests were conducted at three levels of the collector concentration and two levels of the frother concentration in a wide pH range from 2 to 12, with increments of two pH units. Additional tests were made at pH 11 for some critical conditions.

## RESULTS

Micro-flotation recoveries (micro-floatabilities) of pure minerals, rutile and zircon, are plotted in Figs. 1 and 2, respectively, as a function of pH, at three levels of Na-Ol concentration and two levels of frother concentration.
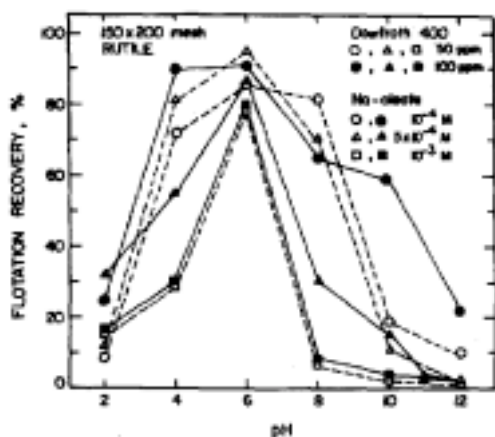


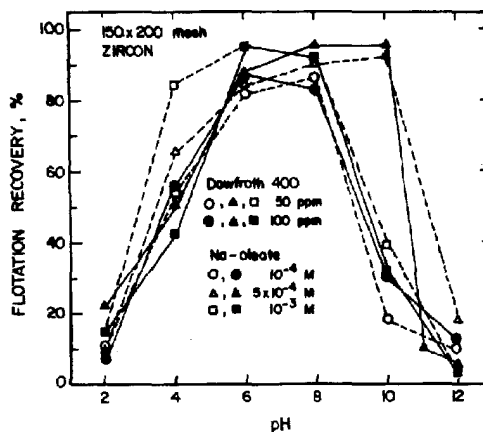Fig. 1. Floatability of rutile with sodium oleate as a function of pH

Fig. 2. Floatability of zircon with sodium oleate as a function of pH

Peak recoveries of rutile were achieved at pH 6 with Na-Ol for all the concentration levels tested, irrespective of the frother concentration. The floatability of rutile, however, decreased significantly with increasing and decreasing pH around 6; the decrease in the floatability being sharper with increasing concentration of the collector Na-Ol. The lower and the upper critical pH values for rutile flotation appeared to depend also on the Na-Ol concentration. The frother concentration, tested at two levels, did not lead to any significant change in the overall flotation trend. Among the conditions tested with Na-Ol, the best flotability for the rutile was determined for the case of $5 \times 10^{-4}$M Na-Ol, 100 ppm frother, and pH 6.

Optimal floatability pH range of the zircon sample with Na-Ol was relatively wider than that of the rutile. Peak recoveries, being a function of the Na-Ol concentration, were achieved at pH values from 6 to 10. The best floatability for the zircon was determined for the case of $5 \times 10^{-4}$M Na-Ol, 100 ppm frother, and pH 10. The decrease in the zircon floatability was much sharper in the strongly alkaline range than the acidic range.

Floatabilities of the rutile and zircon samples with the amine type collector, hydrogenated tallow amine acetate (HTAA), are plotted as a function of pH in Figs. 3 and 4, respectively. The pH range of maximum flotation of rutile was somewhat more sensitive to the frother concentration than that of zircon. Flotation recoveries around 90% were observed in the pH range 6 to 8 for rutile, and 6 to 10 for zircon.

Floatability of both minerals decreased sharply in the alkaline region above their respective critical pH values, pH 8 for rutile and pH 10 for zircon. In the acidic region, rutile indicated a higher degree of floatability than zircon.
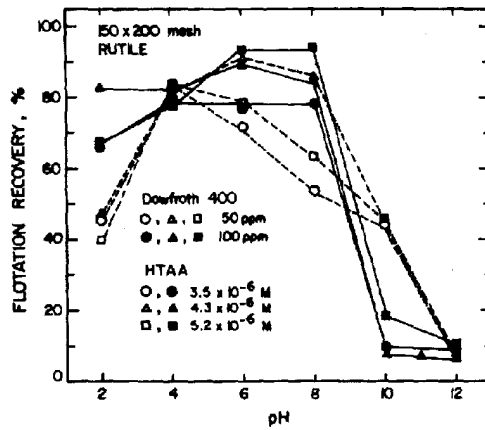


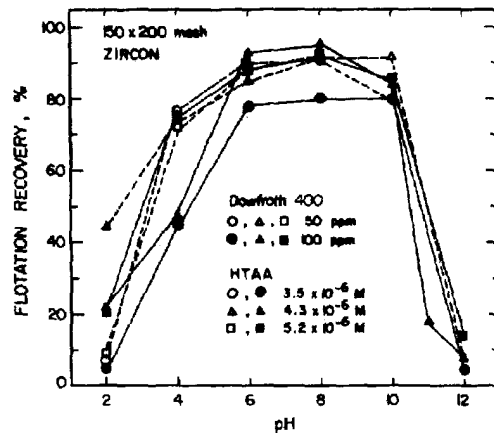Fig. 3. Floatability of rutile with amine as a function of pH



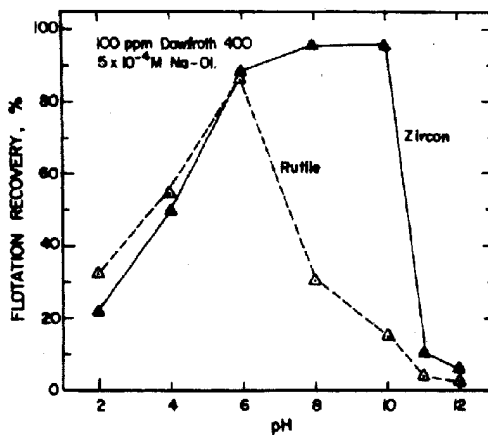Fig. 4. Floatability of zircon with amine as a function of pH



Fig. 5. Floatability of rutile and zircon with sodium oleate as a function of pH.
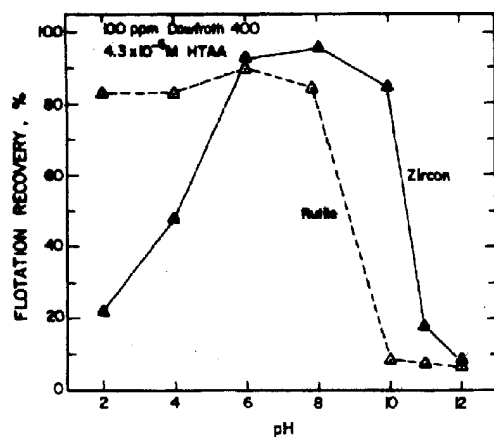


Fig. 6. Floatability of rutile and zircon with amine as a function of pH.

A comparison of the floatability plots of the rutile and zircon mineral samples with the two collectors, Na-Ol and HTAA, are presented in Figs. 5 and 6, respectively. These figures reveal that pH 10 is critical for the likely differential flotation of the two minerals with both of the collectors. A second critical pH for the possible differential flotation seemed to be pH 2 with the use of HTAA.

## DISCUSSION

Even though the differential flotation from a mixture of rutile and zircon had not been tested at the time of writing, it is apparent from the present study that the selectivity between these minerals should be achieved in the alkaline medium with sodium oleate or HTAA as collector since there seems to be sufficient differences in the upper critical pH values of the minerals in both collector systems.

In sodium oleate-mineral systems, each mineral has a critical oleate concentration for flotation; and the type of collector adsorption (physical, chemical, or a combination) is governed by the solution pH and oleate concentration (Drzymala and Lekki, 1992). According to the data on oleate species distribution as a function of pH (Pugh and Stenius, 1985; Drzymala, 1985), the molecular precipitated oleic acid is the predominant species at low pH (<5); monomer oleate ion and oleate dimers predominate in the alkaline range pH> 8.There also exist relatively low concentrations of the intermediate ion-molecular species,$(RCOO)_2H^-$, at pH 8. At pH>5 and <7.5, molecular and ionic oleate species co-exist in relatively more abundant concentrations.

In view of the oleate species distribution data and the negative zeta potential of the mineral particles, the maximal flotation of rutile at pH 6 in the present study can be attributed to adsorption of molecular precipitated oleic acid (RCOOH) and oleate ion (RCOO$^-$). Even though the mechanism of adsorption is still unclear, it has been generally agreed that the initial adsorption step involves the chemisorption of the oleate ion bound to the lattice cation so as to create optimal conditions for the physical adsorption of other collector species. Abramov (2000) proposed that effective flotation takes place only when there is an optimal ratio of chemisorbed and physisorbed collector species, while the former provides hydrohopization of the surface and the latter ensures kinetic functions (effective film rupture) of air bubble-particle attachment.

In the case of the oleate/zircon system, the maximal floatability starts at pH 6 but, in contrast to the rutile system, extends further into the alkaline region (pH 10), and drops sharply above pH 10. The co-existing collector species in the mid-pH range 6 to 10 are predominantly monomer and dimer oleate species, and, in relatively much lower concentration, the ion-molecular species. Although the ion-molecular species has been claimed to promote the co-adsorption and flotation with other collector species (Ananthapadmanabhan and Somasundaran, 1981), this species cannot be held responsible for the floatability of the mineral samples in the present study since its effect as such is absent in the case of rutile. It is very likely that specific adsorption of monomer and dimer oleate species led to flotation in the mid-pH range. The predominant species in the strongly alkaline range (pH>10), where a sharp decrease in the zircon floatability was observed, are also monomer or dimer oleate species. This sharp floatability decrease in the strongly alkaline range can be plausibly attributed to overwhelming competition of OH$^-$ ions for surface sites against the chemisorbing anionic monomer or dimer oleate species.

The striking difference between the upper critical pH of flotation of rutile (pH 6) and that of zircon (pH 10) should be explicable by the differences in their crystal chemistry and surface properties. Flotation in chemisorption systems of oxides and silicates is said to be related directly to the formation of hydroxy complexes of metal ions (or their reduced species) comprising the mineral (Fuerstenau and Palmer, 1976). It seems, therefore, plausible to suppose that the difference in the upper critical pH of the two minerals arises from the differences in their extent of surface hydroxylation and the stability of the water of hydration around the particle surfaces, with which the collector species compete.

In the case of the amine system, the difference in the upper critical pH values of the two minerals was diminished. The critical pH for zircon was again 10, as in the oleate system, but that of rutile shifted to pH 8. According to the amine species distribution diagram (Pugh, 1986), the quantities of ionic amine (aminium ion) and the ion-molecular complex $RNH_2.RNH_3^+$ are maximum at around pH 10, and both decrease rapidly with increasing pH. Most researchers are in agreement that amines are physisorbing collectors for oxide and silicate mineral surfaces. Physical adsorption of the aminium ion and a synergistic co-adsorption of neutral amine molecules and/or the ion-molecular complex are believed to be the major mechanism of the surface hydrophobization. The sharp cessation of flotation at high pH values in amine systems has been attributed to diminishing ionic amine concentration and, at the same time, to competion from the increasing $Na^+$ concentration from the added NaOH.

The upper critical pH of flotation (pH 10) for the silicate mineral zircon of the present study coincides with the maximum flotation pH of quartz with amines, reported in an earlier study (Bleier et al., 1976). It seems reasonable to suppose that the difference in the upper critical pH values of the rutile and zircon is mainly due to the silica tetrahedra in the structure of the latter mineral so that its surface behaves as if it were a mixed oxide made up of silica and metal oxide. The silica part controls the floatability in the pH range 8 to 10.

## CONCLUSIONS

Sodium oleate and hydrogenated tallow amine acetate were efficient collectors for rutile and zircon. Zircon floated better over a relatively wider near-neutral and basic pH range than rutile with both of the collectors, probably due to its mixed metal oxide-silica surface structure. Rutile floated reasonably well in the pH range 2 to 8 with the amine collector, but yielded a peak floatability at pH 6 with the oleate. The upper critical pH values of flotation were:10 for zircon with both of the collectors; 6 for the rutile/oleate system, and 8 for the rutile/amine system. Differential flotation of the two minerals seems possible at pH 10. Further research has been undertaken to float minerals from their mixtures in the absence and presence of an efficient depressant.

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Flotowalność czystych minerałów rutylu i cyrkonu badano przy pomocy testów mikroflotacyjnych. Kolektorami w procesie flotacji były oleinian sadu i octan talowej aminy. Badania flotacyjne prowadzono w zakresie pH od 2 do 12, stosując trzy różne stężenia kolektora i  dwa stężenia odczynnika pianotwórczego (glikol polipropylenowy). Rutyl wykazywał maksimum flotowalności przy pH 6, przy użyciu jako kolektora oleinianu sodu. Stosując kolektor aminowy dobre wyniki flotacji rutylu uzyskano w zakresie pH od 2 do 8. Wyraźny spadek flotowalności obserwowano przy pH>8. Maksymalna flotowalność cyrkonu, przy użyciu obu kolektorów, była w zakresie pH 6-10. Flotowalność cyrkonu malała szybko przy pH>10. Równie, wyraźny spadek flotowalności cyrkonu obserwowano w środowisku kwaśnym pH poniżej 6. Otrzymane wyniki z flotacji zostaly przedyskutowane w oparciu o prawdopodobne mechanizmy adsorpcji badanych kolektorów do powierzchni minerałów. Różnice w flotacji minerałów w obszarze alkalicznym sugeruja możliwość separcji tych minerałów przy zastosowaniu badanych kolektorów flotacyjnych.