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Short communication

Batch sedimentation of magnetic flocs in a magnetic field

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Abstract

This paper examines the magnetic and sedimentation properties of a synthetic magnetite developed for water treatment. This was made by the precipitation of a mixture of ferrous and ferric ions with sodium hydroxide at room temperature. The ferrous to ferric ratio was varied between 0.2 and 3.0. Its magnetic properties were compared with iron and other magnetic materials. Experiments show that a permanent magnet placed at the bottom of a settling apparatus greatly speeds up the sedimentation rate in a vessel of 30 cm height. The best range of ferrous to ferric ratio to obtain a high sedimentation velocity is from $\frac{1}{3}$ to $\frac{2}{3}$.

Keywords: Batch sedimentation; Magnetic flocs; Water treatment

1. Introduction

The ‘Sirofloc’ process, developed in Australia for potable and waste water treatment, uses a magnetic material to remove impurities from the feed [1]. This process takes place at a fairly low pH (around 5.5). The loaded magnetic material is then treated with NaOH and the pH is raised to 9.5. This releases the impurities and thus the magnetic material can be removed by a magnetic separator and returned to the head of the process [2]. The magnetic material used is finely ground mineral magnetite which is quite costly and which must be recovered effectively to keep down process costs [3]. Recycling of this reagent also implies that impurities, especially micro-organisms, may build up in the plant. There is consequently some interest in making cheaper reagents with a lower magnetic recovery in the circuit.

Over the last 2 years our laboratory has been developing a magnetic flocculant that can be made using a simple apparatus for use in water treatment [4]. In this case a mixture of ferrous and ferric ions is precipitated at room temperature with sodium hydroxide to form a precipitate that is magnetic [5]. No previous research was done on the magnetic properties of these precipitates and this will be the main aim of the present paper. Firstly the measurement of the magnetic attraction forces of these flocs will be compared with other magnetic materials. The second aim is to compare the batch settling properties of the materials both under gravity alone and in the case where a permanent magnet is placed at the bottom of the batch settling tester [6].

2. Determination of magnetic forces

The first part of the experimental work was carried out to determine the force exerted upon dry magnetic materials and to determine the particle size of the flocs in aqueous suspension. Several synthetically precipitated ‘magnetic flocs’, with varying ferrous to ferric ratios, were washed, air dried and tested in air in a simple apparatus which is shown in Fig. 1. To produce these flocs, known amounts of ferrous chloride and ferric chloride were added to distilled water which had been pre-heated in a kettle to accelerate dissolution of the salts. A quantity of sodium hydroxide was dissolved separately in distilled water. The hydroxide solution was gradually added to the iron solution with rapid stirring and made up to 1 l with distilled water. Natural magnetite ore was also tested.

The apparatus used for measuring the magnetic force consisted of a top loading balance that was placed in a rigid frame. A cradle consisting of a support and string held the sample in a small plastic container. This was placed at a height h above the magnet. This height was measured using a metric ruler and the weight on the balance was recorded. The data obtained was correlated as shown below.

When no magnetic field is applied to a mass m of ferromagnetic particles, the force on them (F_N) is simply due to

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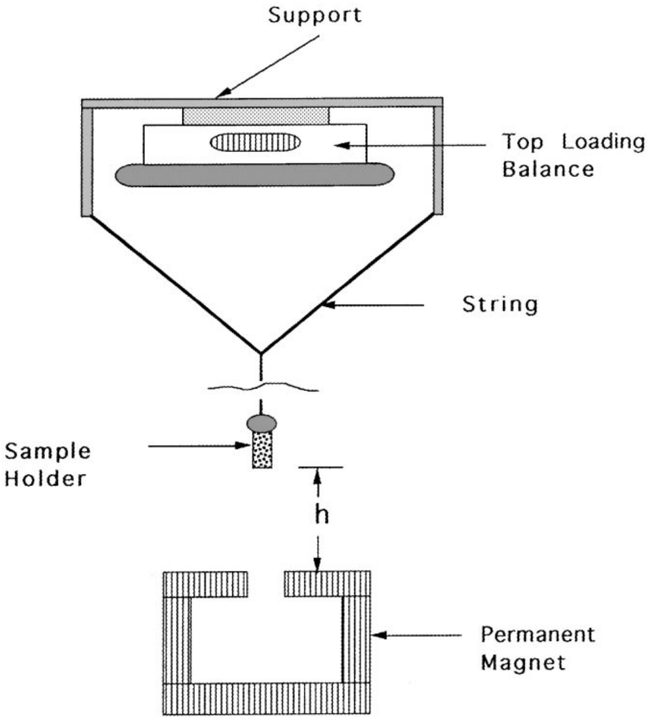

Fig. 1. Apparatus for determining magnetic properties.

gravity alone. Therefore

$$F_N = mg \tag{1}$$

Here m is the sample mass and g is the gravitational constant. When a magnetic force is applied to the sedimentation column, the force on this increases for magnetic materials. If an inverse square law is applicable for the effect of magnetism on the floc, then the force on the sample in a magnetic field (F_M) is given by

$$F_M = mg + \frac{mk}{h^2} \tag{2}$$

In this expression, h is the height of the sample from the top of the magnet and k is a constant. This would assume that the magnet was a point source and that

$$\frac{F_M}{F_N} = 1 + \frac{k}{gh^2} \tag{3}$$

Fig. 2 gives a typical example of F_M/F_N vs. $1/h^2$ data and it seems that they correlate smoothly. The assumption that the magnet is a point source and that an inverse square law is applicable seems to be reasonable.

In order to reduce this data, a magnetic attraction factor f was used to estimate the degree of magnetism of the magnetic materials. Natural magnetite, one of the most magnetic of the materials studied, was assumed to have an f value of unity. f is the ratio of the slope of the magnetic flocs prepared ('k' of Eq. (3)) to that of natural magnetite.

The 'f' values of the magnetic flocs prepared in this experimental work are plotted in Fig. 3 as a function of the starting ferrous to ferric ratios. Note that h was measured between the bottom of the container and the top of the magnet (Fig. 1). For bulky samples a small constant correction factor (about 1 cm) had to be added to h to allow for this and to obtain straight line plot against $1/h^2$. The actual ratios studied in this investigation were 0.2, $\frac{1}{3}$, $\frac{2}{3}$, 1.0, 1.5, 2 and 3.

As expected at the lowest value of the ferrous to ferric ratio, the f value was the lowest at around 0.4. For the value of $\frac{2}{3}$, f had risen to 0.85. At higher values of the ferrous to ferric ratio, even higher values of f were measured and it reached 0.99 when the ratio was 2 before falling when the ratio was 3. These runs were repeated and the results confirmed. It is probable that significant oxidation of ferrous ion was responsible for this as no stabilising compound was added and the samples were left to dry in air for at least 24 h. Ferrous salts are cheaper than ferric salts as they do not have to be oxidised. Therefore the results given in Fig. 3 could be of economical importance.

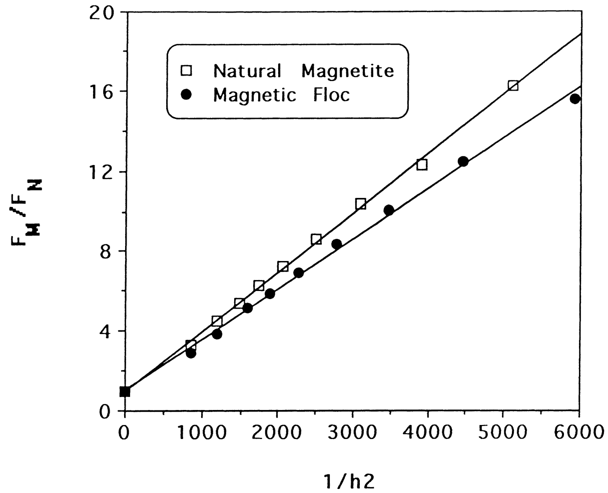

Fig. 2. Sample magnetic force results.

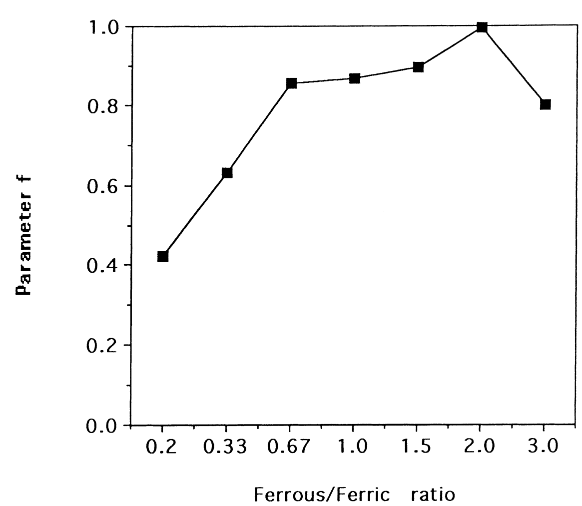

Fig. 3. Results for the magnetic 'f' parameter.

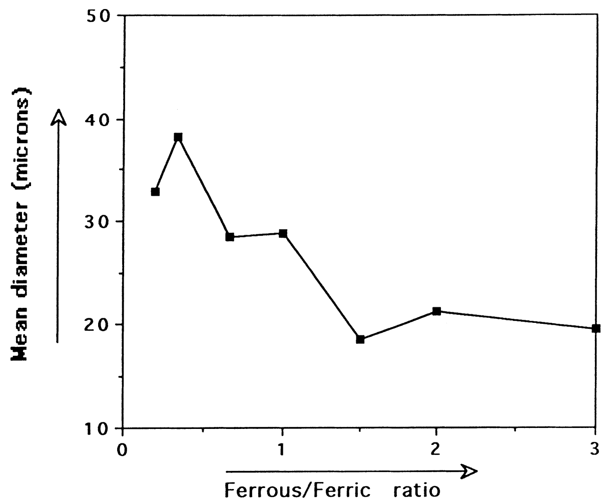

Fig. 4. Mean floc sizes.

Sizing of the magnetic flocs in aqueous suspension were done using a 'Malvern' laser operated particle sizer. The particle sizes of the natural 'ground' magnetite and the synthetic one were also measured. In the normal operation of this instrument, the sample is put in a cell which is stirred with a magnetic stirrer. However, the presence of the magnetic stirrer caused magnetic particle to attach to it. For this reason a cell attached to a small pump was used for the measurements as shown in Fig. 4. The general trend shows that the floc size decreases from 40 to around 20 μm as the ferrous to ferric ratio increases. The particle size of the natural magnetite was in the same range at 22 μm but the synthetic magnetite (BDH 'AnlaR') was much smaller at 7 μm.

3. Settling tests

In this series of experimental tests freshly prepared flocculant was placed in a cylindrical container. The container was a tube of glass with 15 mm internal diameter and 30 cm height which was sealed at both ends with rubber corks. The tube was small enough to be placed between the poles of the permanent magnet so that the bottom of the settling apparatus could be aligned accurately with the top of the magnet. The total initial concentration of iron was held constant at 10 g/l. Two sedimentation tests were carried out simultaneously — one with the magnet present and the other without. Before the test started the container was well shaken to ensure that the contents were well mixed and then a ruler was inserted into the cylinder to stop the fluids swirling around. A standard settling test was performed and the height h of the slurry water interface was measured as a function of time t.

In an initial experiment, sedimentation of the natural finely ground magnetite was studied in the presence of the permanent magnet. The results of this experiment are shown schematically in Fig. 5. Immediately after the sedimentation container was placed on the magnet, the magnetite at the bottom rapidly settled under the attraction of the magnet.

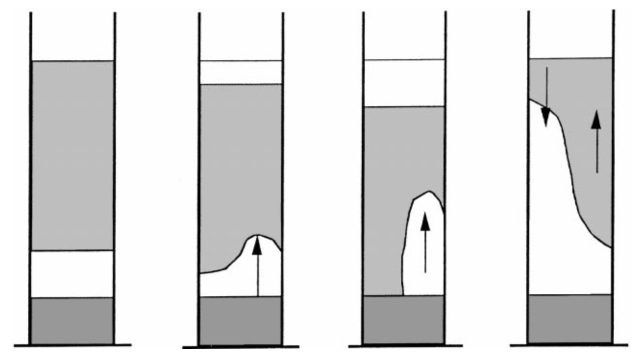

Fig. 5. Unstable sedimentation in a magnetic field.

This caused the momentary formation of a zone of clear water under the more dense slurry above as is shown in the left-hand side illustration. The interface broke as the less dense fluid rose to the top and this caused an instability in which most of the magnetite sank rapidly to the bottom.

Sedimentation tests were carried out with all seven values of the ferrous to ferric ratio used earlier for the magnetic force tests. A typical set of data is shown in Fig. 6. The sedimentation rate when the magnet was present was much larger than settling under gravity alone. The general shape of the settling under gravity alone data is typical with the settling velocity gradually decreasing with time. For the magnetic assisted tests the settling rate was constant for most of the time and then it suddenly decreased.

The initial settling velocities for both sets of runs are shown in Fig. 7. In general the initial settling velocities for the magnetically assisted sedimentation runs are double of those for gravity alone but the best results for the largest settling rates occur when the ferrous to ferric ratio is either $\frac{1}{3}$ or $\frac{2}{3}$. From Fig. 4 it can be seen that these flocs have the largest size. The maximum sedimentation velocity measured with the synthetic flocs was 0.38 mm/s. A gravity test with ground natural magnetite showed an initial settling velocity of 4 mm/s which is much more rapid than for the flocs. The

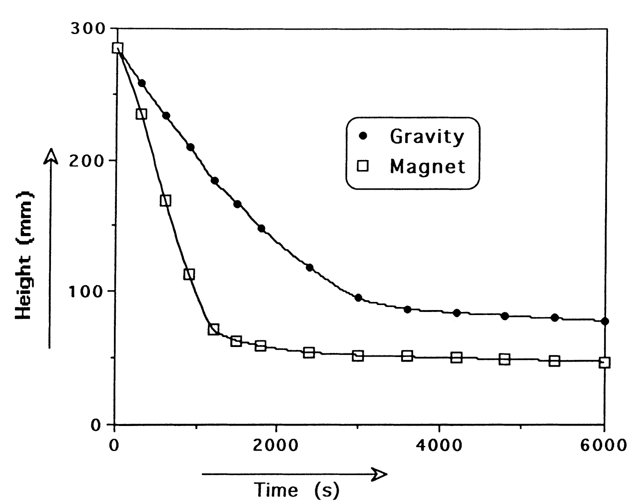

Fig. 6. Typical sedimentation data.

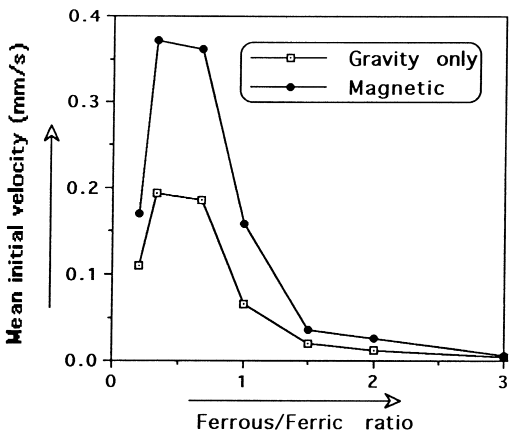

Fig. 7. Initial settling velocities.

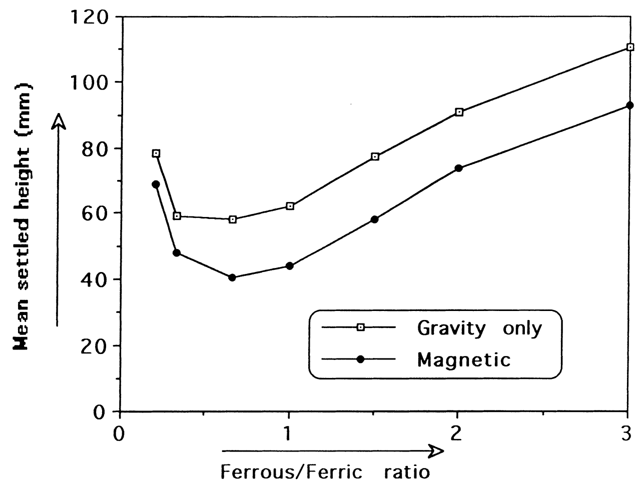

Fig. 9. Final settled heights.

sedimentation rates for high values of the ferrous to ferric ratio are less than one-tenth of those for the cases where this ratio is either $\frac{1}{3}$ or $\frac{2}{3}$, although the data given in Fig. 3 shows that the dried particles are magnetic at the higher ratios.

It was initially hoped that the sedimentation velocity data could be correlated in some way to show the effect of a magnetic field. The problem is that the data are not reproducible. The problem is shown in Fig. 8 where some runs for the floc with a ferrous to ferric ratio of 0.5 is given. In these experiments the sedimentation runs were repeated three times. One batch of floc was placed on the magnet and another was allowed to settle under gravity. In each case the initial settling velocities were measured. For the gravity settling runs some sort of reproducibility was noted in all but the first run. In the magnetic tests the initial velocity continued to rise quite significantly and suggest that the flocs were coalescing in the magnetic field. It should be noted that similar results were obtained for the other flocs.

Finally the mean settled heights for the sedimentation tests are given in Fig. 9. The contents of the sedimentation vessels were left to stand for at least 20 h before these measurements were done. In all cases it is seen that the settled volumes for sedimentation under a magnetic field are smaller and this indicates the magnetic nature of the flocs. The most important point to note is that these measurements confirm that the floc prepared at the higher ratios of 1–3 have significant magnetic properties. However, the fact that the settled volumes increase steadily in this range show that the flocs precipitated when the ferrous to ferric ratio is 1.5–3 contain large quantities of water. Hence their densities will be significantly lower than those with this ratio in the region of 0.33–1.

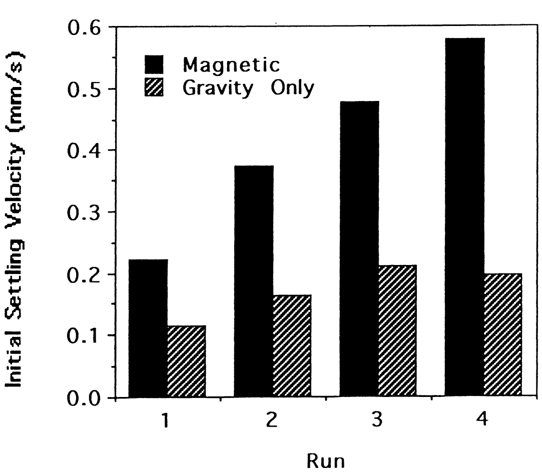

Fig. 8. Reproducibility of data.

4. Conclusions

The most important result of the present investigation shows that flocs prepared when the ferrous to ferric ratio is $\frac{1}{3}$–$\frac{2}{3}$ have the highest settling velocities. This velocity is significantly higher when settling is carried out in a magnetic field and it increases if the same floc is used for two or more times. The magnitude of the slurry sedimentation velocity of a floc in a magnetic floc is determined by three parameters

1. the magnetic properties of the floc,
2. the floc diameter,
3. the density difference between the flocs and the surrounding free water.

There is no reason to suspect that there will be a great variation in the last parameter and Fig. 3 does not show much variation in the first. So floc size would seem to be the most important one.

The results of this paper show that the disadvantage of the synthetic magnetic flocs is their low settling rate and their high settled volumes when compared to natural magnetite. However, it could be possible to increase their size by conditioning in a magnetic field as the results in Fig. 8 would indicate. However, future work should be carried out with a ferrous to ferric ratio of 0.5 only using flocs precipitated in situ. A future development could consider the use of dried synthetic magnetite. An important factor here would be the relative costs between the finely ground magnetic material presently used and the dried precipitated material made in this work.

5. Nomenclature

f	magnetic constant
F_M	magnetic force
F_N	normal gravitational force
g	gravitational constant
h	height above magnet
k	constant defined in Eq. (2)
m	particle mass

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