

WATER TREATMENT WITH RECYCLABLE MAGNETIC MICROPARTICLES

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Abstract Magnetic microparticles with reactive surfaces can be used to rapidly remove soluble and insoluble materials from water with the aid of novel contacting systems. This paper reviews work on the development of a new process, which uses specially pretreated finely divided particles of magnetite to remove colloidal material from a raw water. This process has now reached the commercial stage, with the design, construction and operation of a 35 Ml/day demonstration plant.

INTRODUCTION

The increasing stringency of water pollution control, along with an ever-increasing demand for high quality water for domestic and industrial use, requires more sophisticated treatment processes. Conventional techniques are relatively slow and facilities for the treatment of massive volumes of water take up large areas of land. There is a need, therefore, for new, faster processes.

The magnetic particle concept, which exploits the rapid reaction rates of very small particles, has been successfully developed by CSIRO in a number of water treatment areas, with the use of simple contacting techniques well suited to very large scale operation. The method was first used in the ion-exchange area as a means of overcoming the difficulties associated with the handling of very fine particles¹. This approach led to the development of a simple pipe reactor, which has been tested in a pilot plant for the dealkalization of a non-clarified waste water². Non-functional magnetic polymers have also been used in hydrophilic forms as reusable filter aids³, and in hydrophobic forms as a vehicle for

the recovery of oil spills in harbour waters⁴.

In the clarification area, it has been found that magnetic cation-exchange resins loaded with aluminium ions can be used to soften and clarify a hard, turbid water⁵. The resins acted as nuclei for flocculation, after calcium ions in the water were exchanged for aluminium ions, which destabilized and coagulated colloids in the usual way. However, dissolution and recycle of the precipitated aluminium hydroxide was not found to be feasible in practice.

Finely divided solids such as silica, bentonite and other clays have been used by other workers in the past, in conjunction with a primary coagulant, to accelerate the clarification process and to obtain a higher quality product water⁶. The use of magnetic particles on a similar "throw away" basis has recently been proposed elsewhere⁷, with the emphasis on the application of high gradient magnetic separators (HGMS). Achievements in this area have been summarized by de Latour⁸⁻¹⁰, who concluded that magnetite particles of size 0.1 to 10 μm can be used, with a primary coagulant such as alum or calcium chloride; the magnetic particles act as a seeding material to which the non-magnetic impurities in the water become attached, so that they can be removed by means of a HGMS. In certain applications, this allows the use of extremely high flow rates, up to 23 cm/s (350 US gpm/ft²). Besides removing inorganic colloids, this method can also remove biological contaminants such as bacteria, virus and algae. A preliminary economic analysis indicated that the current cost of the HGMS method for 80-90% solids removal from municipal secondary effluent would be 6 cents US/m³ for plants of 3600 m³/day capacity (22 cents per 1000 US gallons for 10 Mgd). This was said to be economically competitive with conventional two-stage tertiary lime treatment. An important advantage is the relatively small size of the treatment facilities, because of the large throughput of the HGMS process.

The present paper reviews work in CSIRO on the use of specially prepared magnetic particles for the removal of both

suspended solids and dissolved coloured material in the one treatment step. The regeneration and reuse of the particles is an inherent feature of the process, which gives it a distinct economic advantage.

EARLY STUDIES

The graft polymerization of quaternary ammonium monomers on magnetic polymeric cores yields particles consisting of iron oxide embedded in a crosslinked bead to the surface of which is attached a multitude of polymer chains of "whisker"-like molecular form¹¹. These positively charged whiskers are extremely effective in adsorbing suspended matter which, in general, has a net negative charge, such as clays, algae and other particles present in natural water and wastewaters. Dissolved coloured material, which exists as anions, is removed simultaneously to levels formerly attained only with "scavenger" ion-exchange resins. However, conventional resins of the quaternary ammonium type, despite their positive charge, adsorb suspended solids poorly. This was originally ascribed to the rigid structure of these resins, in contrast to the deformable surface of the "whisker" resins, which is soft and may allow the active chains to attach themselves to the adsorbed particle at many locations. However, further investigations showed that the ability of the resins to adsorb colloids was determined by particle size.

Regeneration of the resin is achieved with brine and caustic soda. Unfortunately, the cost of preparing the whisker resins is quite high, as is that of the caustic/brine regeneration. Cheaper ways of obtaining the charged magnetic particles were therefore sought.

Ferric hydroxide exhibits an increasing positive charge with decreasing pH, its point of zero charge being at about pH 7.2. As ferric hydroxide is essentially insoluble between pH levels 4.5 and 10.0, there exists a range of pH values where the surface charge is positive in nature. Whereas freshly precipitated ferric hydrox-

ide dissolves rapidly in acid, a boiled or aged precipitate dissolves much more slowly; this indicates further insolubilization arising from crosslinking via Fe-O-Fe bridges.

It was found¹² that particles of magnetite could be coated with a layer of polymerized ferric hydroxide by suspending the particles in water, adding ferric chloride, and raising the pH to 10.5 by the addition of alkali. These particles were very effective at adsorbing turbidity and colour colloids, but did not have sufficient mechanical strength to allow long-term regeneration and reuse. A search for a more robust particle led to a study of the surface properties of magnetite particles.

BASIC PHENOMENA

Many solid materials when finely divided and suspended in water develop a surface charge, the sign of which is normally dependent on the pH level. Naturally occurring magnetite (Fe_3O_4) is generally negatively charged due to the presence on its surface of small amounts of silica, a ubiquitous contaminant of mineral matter. A plot of electrophoretic mobility versus pH for such a material is given in Figure 1 and it can be seen that the material is negatively charged at all pH values above 3.6, the iso-electric point (i.e.p.).

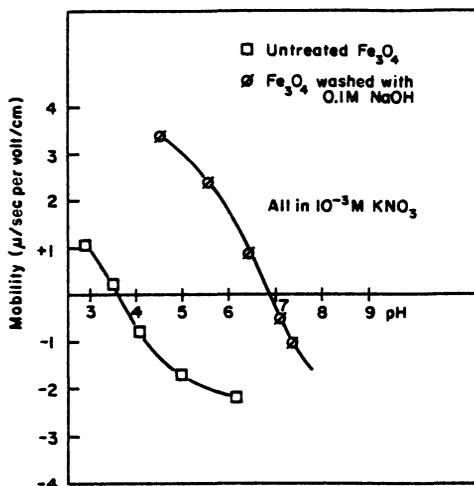
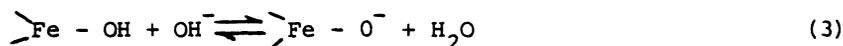
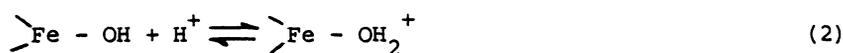
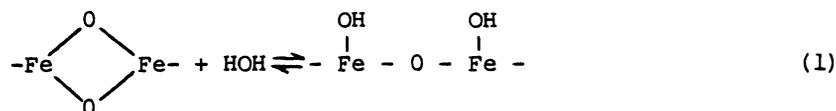


FIGURE 1 Mobility vs pH for raw and treated magnetite.

On the same diagram is also plotted a curve for magnetite particles which have been washed with a 0.1M sodium hydroxide solution, and it can be seen that the i.e.p. has moved to a pH level of about 7.0. Consequently, under acidic conditions this magnetite surface will carry a net positive charge. The sodium hydroxide wash removes silica and other impurities from the magnetite surface leaving a clean metal oxide which can develop a charge as outlined in equations 1 to 3.



It was found in jar test experiments¹³ that pretreatment of very finely divided magnetite (size 1-10 μm) with sodium hydroxide greatly increased its capacity to adsorb colloidal material. Some typical results are given in Table 1.

TABLE 1 Effect of pretreatment on the ability of magnetite to adsorb colloidal matter.

Pretreatment Used	Coagulant Added	Product Water	
		Turbidity (NTU)	Colour (Pt-Co)
NONE	20 mg/l alum alone	5	30
NONE	12g/l of Fe ₃ O ₄ +20mg/l alum	4	25
0.1M NaOH	12g/l of Fe ₃ O ₄ +20mg/l alum	1	5
Acid (pH 2.5)	" " " "	6	35
Lime (pH 12.0)	" " " "	12	50

Raw water: Turbidity (T) = 33 NTU, Colour (C) = 70 Pt.Co. units. All jar tests carried out at pH = 5.5.

All experiments included a constant dose of 20 mg/l of alum. In the absence of alum the difference in performance between treated and untreated magnetite is even greater. Table 1 shows that acid regeneration of the magnetite is ineffective and that the use of lime is markedly detrimental. Particle size of the magnetite is another important parameter (Table 2). The data indicate that the process is controlled by the magnetite's effective surface area; the smaller the particle size the better is its performance. Difficulties in preparation and handling precluded the use of submicron magnetite, so particles in the 1-10 μm size range were utilized.

TABLE 2 Effect of particle size on process efficiency.

Magnetite dose g/l	Particle size of magnetite (μm)	Product Water	
		Turbidity (NTU)	Colour (Pt-Co)
NIL	(raw water only)	21	28
12	15 - 20	17	25
12	6 - 15	14	22
12	1 - 5	3	4

Jar test conditions: pH = 5.0, no additional coagulant.

The basic mechanism of the process depends on the ability of a positively charged magnetite surface to neutralize and adsorb negatively charged colloids. If the pH level is then raised above the isoelectric point of the magnetite with sodium hydroxide, the magnetite surface becomes negatively charged and the attached colloids are repelled. Consequently, the magnetite particles are capable of acting as a coagulant/adsorbent at low pH, can be regenerated at high pH, and then reused.

PROCESS DEVELOPMENT

A clear picture of the basic steps in the process, as carried out in jar tests, can be obtained from the process block diagram shown in Figure 2.

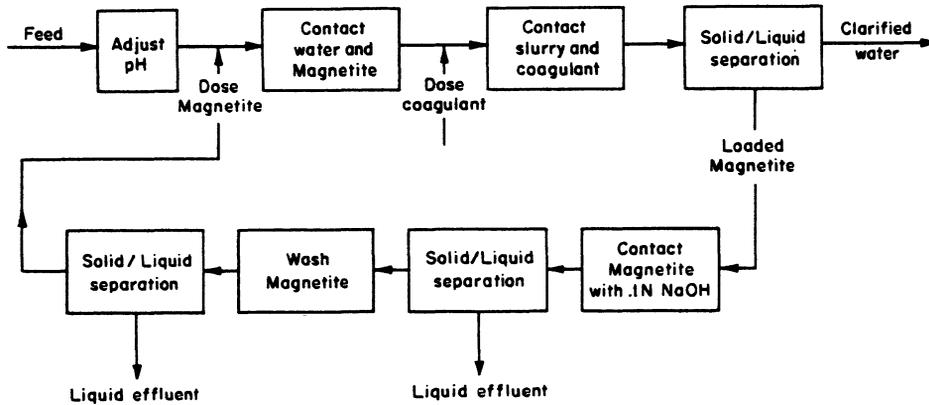


FIGURE 2 Process block diagram.

Initially, the feedwater pH is adjusted to the optimum value for the process. This can vary from 5.0 to as high as 8.5 depending on the particular water, although, in general, the lower the pH the better the performance. Subsequently, the water is dosed with freshly regenerated magnetite slurry at a rate which can vary from 0.5 to 2.0% w/w of the raw water flow. The magnetite must be demagnetized before addition; otherwise, it clumps together and does not present its full surface area to the water. The first period of contact time between water and magnetite can vary from 5 to 10 min., during which colour bodies in the water (mainly humic and fulvic acids) are destabilized and adsorbed on to the magnetite surface. There is also some reduction in turbidity. Prior to the second period, a polyelectrolyte is dosed at a rate which can vary from 0.1 to 2.0 mg/l, depending mainly on the level of turbidity in the raw water. Polyelectrolyte is used exclusively as the secondary coagulant, in lieu of alum as described in earlier work¹³. During the second period, which can vary in length from 2 to 4 min., final traces of colour are removed, and the polyelectrolyte firmly binds the remaining turbidity onto the magnetite surface. Total contact time in the process can vary from 7 to 14 min.

The contact steps are followed by separation of the magnetite from the clarified water, which now has a turbidity generally less than 1 NTU and colour less than 5 Pt-Co units. The magnetite is then cleaned and regenerated prior to reuse, and it is these steps which make the process unique. Magnetite has been used before in water treatment, but only as a floc weighting agent and on a once-through basis. The magnetite used in the CSIRO process, after regeneration with caustic soda, acts as a coagulant in its own right and can eliminate the requirement for conventional coagulants such as alum or ferric chloride. In regeneration two different phenomena occur. Firstly, the turbidity and colour bodies are stripped off the magnetite and, secondly, the magnetite slurry is washed. Regeneration requires a pH level in the range 11-12, while the washing step is usually carried out at a pH level between 10 and 11. An intensive period of process development work, which has been described elsewhere^{14,15} resulted in the process design shown in Figure 3. This formed the basis for the construction and operation of a fully continuous pilot plant capable of treating 60 l/min of raw water.

Contact of the raw water with the demagnetized regenerated magnetite is achieved in a series of four stirred tanks with gravity flow of the slurry between the tanks. Acid is added to the inlet of the first tank for pH adjustment, while polyelectrolyte can be added to the inlet of either the third or fourth tank. From the fourth tank the suspension passes between the poles of a pair of permanent flocculating magnets prior to entering the feed-well of a conventional clarifier. The magnetite is magnetized, and in the feedwell the individual particles attract each other to form large flocs which settle rapidly at rates around 100 m/hr. However, because of the random nature of floc formation, a small but significant number of flocs have much lower settling velocities and, to achieve a product water with a suspended solids content of less than 1 mg/l, the clarifier is designed with an upflow rate of around 10 m/hr.

As shown in Figure 3, regeneration and washing of the magnetite are achieved in a three stage countercurrent flow process in which

the regeneration step (tank T6) is placed in between two washing stages (tanks T5 and T7). Regeneration is placed in this intermediate position so that the high pH water from the washing step following regeneration can be used to raise the pH level of the loaded magnetite coming from the clarifier. This results in an effluent of lower pH and a possible saving in sodium hydroxide use.

The selection of magnetic drum separators for the solid/liquid separation step in each stage was crucial to the success of the washing operation. While the humic and fulvic acids, which comprise the colour, are easily washed from the magnetite surface, the larger clay colloids, which cause the turbidity, are more

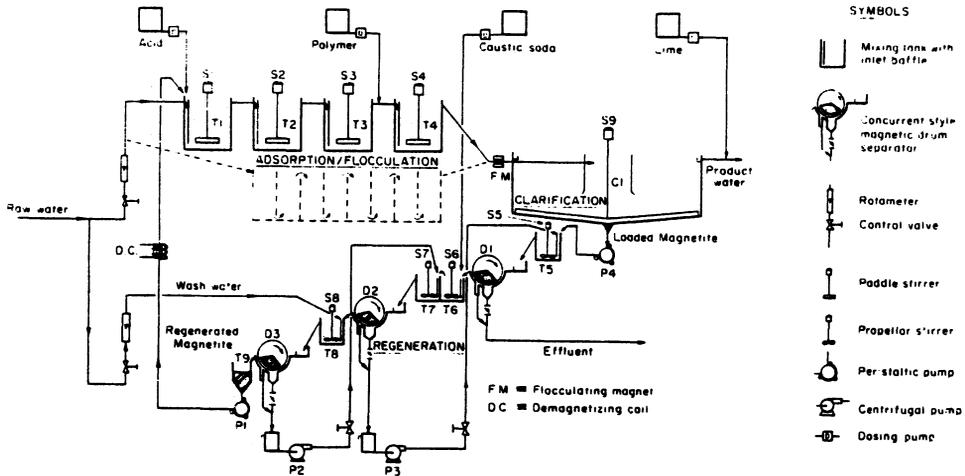


FIGURE 3 Process design.

difficult to remove. The magnetic drum separator, with its combination of mixing turbulence and magnetic field gradient, is capable of providing an efficient separation. Fortunately, such separators have been well developed in the coal washing industry where they provide a cheap and reliable technique for recovering magnetite.

TABLE 3 Pilot plant operation on various waters

Raw Water		Pilot Plant Conditions			Product Water Characteristics
Location	Characteristics	pH	magnetite dose g/l	polymer dose mg/l(active)	
Perth, West Australia	anaerobic groundwater, pH=6.1 T=5-20 NTU, C=60-100 Pt.Co units Fe(sol)=1-2 mg/l, H ₂ S=1-2 mg/l	6.0	15	1.0	T=0.5-1.0 NTU, C=6-10 Pt.Co units, Fe(sol)<0.05 mg/l, H ₂ S=nil
Murray River, South Australia	turbid but colourless river water pH=7.5, T=20-25 NTU, C= 2 Pt.Co units	6.6	9	1.6	T=0.8-1.2 NTU, C=0 Pt.Co units
Nyponga Reservoir South Australia	slightly coloured reservoir water pH=7.0, T=4 NTU, C=60 Pt.Co units	6.0	10	1.0	T=0.8-1.4 NTU, C=8-12 Pt.Co. units

TABLE 4. Comparison of operating costs. (AS 1981)

	Unit Cost \$/tonne	Conventional		Magnetite	
		mg/l	c/kl	mg/l	c/kl
Hydrogen Peroxide	1500	2.0*	0.30	1.2	0.18
Lime Putty (CaO)	252	25	0.63	25*	0.63
Alum	113	77	0.87		
Anionic Polyelectrolyte	4250	0.5	0.21		
Cationic Polyelectrolyte	4570			0.7	0.32
Sulphuric Acid	54			25	0.14
Caustic Soda	245			25	0.61
Chlorine	526	5	0.26	5	0.26
Magnetite	100			12*	0.12
Power	5c/kwh	5kw*	0.02	45kw*	0.16
Sludge/Effluent Disposal			**		0.05
			0.13		
Total			2.42		2.47

* estimated for plant of capacity 35 ML/day

** assumes no secondary treatment of sludge

PILOT PLANT OPERATION

The pilot plant has been operated at a number of sites and has successfully treated a variety of waters as described in Table 3. The major investigation was carried out at the Mirrabooka groundwater treatment plant of the Perth Water Board in Western Australia^{15,16}. It proved the viability of the process in direct comparison with a conventional alum clarification plant. Unlike many surface waters, the groundwater at the Perth site was particularly difficult to treat; it also contained significant levels of both soluble iron and H₂S. After an extended period of operation the pilot plant was capable of consistently producing a good quality product water at an economic price. However, this was achieved only with the aid of a two stage countercurrent flow contacting arrangement for the water and magnetite and the use of a high molecular weight polyelectrolyte.

A comparison of operating costs for the magnetite process and the conventional alum process at the Perth site is given in Table 4. While these costs are not significantly different, design studies indicate that the capital cost of the magnetite process could be 20 to 40 percent lower than that of a conventional plant involving coagulation/flocculation, sedimentation and filtration.

For fairly short periods the pilot plant has also treated a turbid but colourless river water and a high colour, low turbidity reservoir water. Both these waters were easier to treat than the Perth groundwater, and required only a single stage of water/magnetite contact and the use of a cationic polyelectrolyte of low molecular weight. However, some new aspects of the process were also discovered. To achieve turbidities of less than 1 NTU the magnetite added to the process must be thoroughly washed. If poorly washed magnetite is used, product water turbidities will rise to between 1 and 2 NTU. For the turbid but colourless river water, operating costs for the magnetite process are greater than for the conventional process. However, both costs are low, the total treatment costs being dominated by amortized capital costs, and thus,

the magnetite process has an overall superiority. For the highly coloured reservoir water, operating costs for the two processes are similar.

DEMONSTRATION PLANT

The successful operation of the pilot plant plus the projected capital cost advantage resulted in the Australian government financing the design and construction of a commercial-sized demonstration plant. The plant, of capacity 35 Ml/day, is located at the Mirrabooka Groundwater Treatment Plant of the Perth Water Board, and is part of a National Water Treatment Systems Development and Demonstration Centre. The plant is of the same design as the pilot plant, and is treating water of the same type. Photographs of the plant are shown in Figures 4 and 5. Operation commenced in March 1981 with the start-up going very smoothly, and the plant was producing acceptable quality water within a short period of time. It can produce about 5% of Perth's total water supply¹⁷.

The successful operation of the demonstration plant has not only confirmed the ability to engineer the process on a large scale but also has provided valuable information and experience for further engineering development. In this regard, the commercial licencees of the process have successfully tendered for the supply of a 15 Ml/day plant to be installed near the North Esk River in Tasmania.

FURTHER PROCESS DEVELOPMENTS

During the rapid development phase, basic research into aspects of the process chemistry and engineering design was pursued successfully, to improve our understanding of these areas.

The major areas of investigation included:

- (i) the role of polyelectrolyte;
- (ii) the effect of hardness ions in the raw water;
- (iii) two stage countercurrent contact of water and magnetite;

(iv) the development of an improved regeneration process. The results of this work have been presented elsewhere^{18,19} and the knowledge obtained is being incorporated into the design of new plants.

CONCLUSIONS

While the initial application of the process has been in the field of potable water, treatment of various industrial effluents has also been investigated in jar tests¹⁸. Satisfactory treatment was obtained in many cases, and the magnetite particles were also able to adsorb phosphate anions, bacteria and viruses^{20,21}.

Research is continuing into the thermodynamics and kinetics of the interaction of various colloids with the magnetite surface in the anticipation that this will lead to further process improvements.

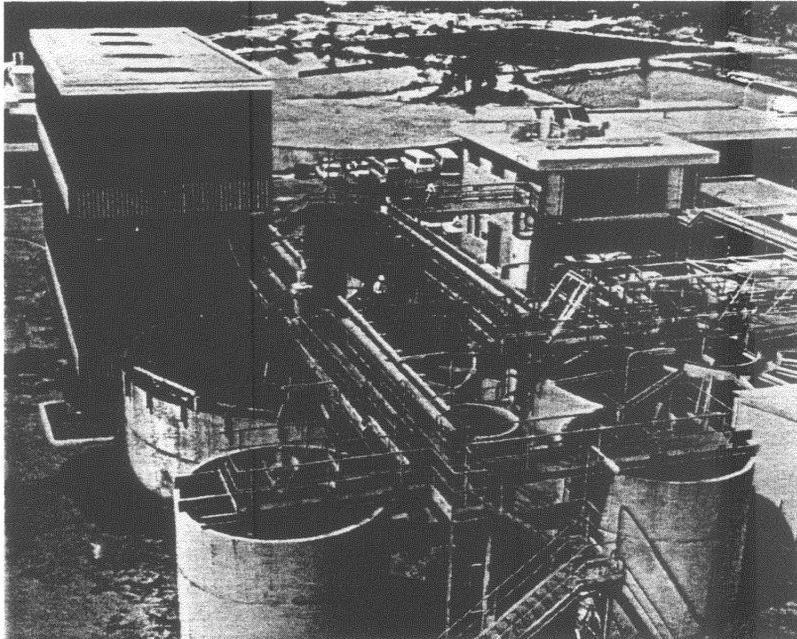


FIGURE 4 Adsorption stages of demonstration plant

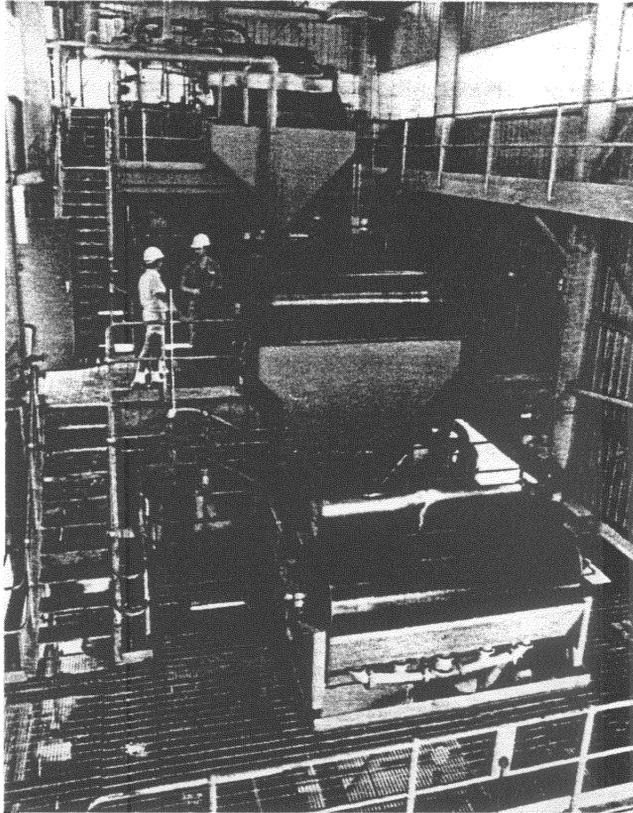


FIGURE 5 Regeneration stage of demonstration plant

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