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A Pilot-Plant Process for Manufacturing Kerosene-Base Ferromagnetic Fluid

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Abstract

A pilot-plant process for kerosene-base ferromagnetic fluid, FMF, has been developed. The chemistry of the process is based on a modified version of the U.S. Bureau of Mines invented peptization process. At the scaled-up volume of the pilot plant, it is capable of producing 4.3 L/h of 0.035 T FMF. The facility could be easily expanded to produce 17.1 L/h of 0.035 T FMF. With the advent of multigap concentrators capable of processing materials of relatively fine particle size (less than 0.5 mm), the FMF saturation magnetizations required are likely to be less than 0.020 T and probably as low as 0.010 T. These FMF concentrations could be obtained by dilution of the manufactured fluids with the base fluid, i.e., kerosene.

I. INTRODUCTION

This paper describes the process for the manufacture of kerosene-base ferromagnetic fluid, FMF, in the pilot-plant facilities of Union Carbide Corporation at Sterling Forest, Tuxedo, New York.

A. Composition of Ferromagnetic Fluid

FMF is a stable, colloidal suspension of magnetite, Fe_3O_4, in a carrier liquid; for example, kerosene. The average size of the magnetite particles is 0.01 μm. Each particle is coated with a monolayer of surfactant molecules; therefore, the tendency of the particles to agglomerate is inhibited and the dispersion is stable. The magnetic nature of FMF is that of a superparamagnet; that is, FMF does not retain any residual magnetization after the

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magnetic field is removed. Sometimes this phenomenon is also called "soft" magnetization.

B. History

Ferromagnetic fluids were discovered at the end of the nineteenth century; however, they soon passed into obscurity. They were rediscovered in the early 1930s when they were prepared by a primitive peptization process. NASA investigated kerosene-base FMF in the early 1960s as a pumpable rocket propellant in microgravity conditions. In the late 1960s AVCO Corporation looked at the possibility of using FMF as a variable density fluid for separation of scrap metals. However, they did not succeed in establishing a commercial process. AVCO also found FMF suitable for seals and today, Ferrofluidics Corporation, formed as a spin-off from the AVCO work, markets, among other things, these seals.

At about the same time as AVCO, the U.S. Bureau of Mines (USBM) became interested in density separations, especially as applied to scrap metals. During the course of this work, they developed the chemistry of a peptization process to manufacture FMF (*1, 2*).

Meanwhile, Union Carbide Corporation in the early 1970s began investigating FMF as applied to density separations. Scarcity and expense of the FMF prompted investigation into various methods of manufacture. Union Carbide Corporation took the bench-scale USBM process, refined it, and scaled it to a pilot-plant operation at its Sterling Forest Laboratories.

The work described in this paper is the scale-up of the laboratory process for kerosene-base FMF manufacture. If the FMF separation technology is to be successful, FMF must be available in large quantities and at a reasonable cost.

The pilot-plant work at Sterling Forest produced some significant improvements over the bench-scale process, the most significant being the development of a mixing procedure which yields a consistently high quality FMF without any appreciable formation of an objectionable emulsion. At its tested capacity, the pilot plant is capable of producing 4.3 L/h of 0.035 T FMF.

II. PROCESS

A. Chemistry

FMF is made by a modified version of the USBM peptization process (*2, 3*). The process description is as follows: Ferrous-ferric ions are reacted with ammonium hydroxide to form a fine (0.01 μm) magnetite (Fe_3O_4) precipitate in an ammonium chloride solution. The precipitated magnetite is contacted with a mixture of oleic acid in kerosene and the entire mass is stirred and heated to 46°C. During this time the excess ammonium hydroxide combines with the oleic acid to form an ammonium oleate soap which coats the magnetite particles. Upon heating to 90°C, the ammonium oleate soap decomposes to oleic acid and ammonia gas. The oleic-acid-coated particles are transferred to the kerosene phase where they remain as a stabilized colloidal suspension, thus forming the FMF. The kerosene phase is separated from the aqueous ammonium chloride by-product by cooling to room temperature and decanting.

The present process yields a product of nominal saturation magnetization of 0.035–0.040 T. Any desired saturation magnetization fluid below this level is obtained by dilution.

The most likely chemical reactions governing the above process are shown below:

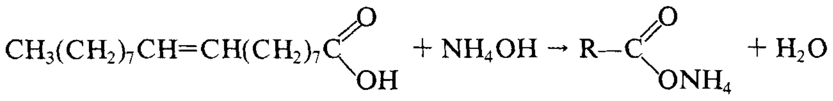
Oxide Precipitation

$$\mathrm{FeCl_3 + 3NH_4OH \rightarrow FeO(OH) + 3NH_4Cl + H_2O}$$
$$\mathrm{FeCl_2 + 2NH_4OH \rightarrow Fe(OH)_2 + 2NH_4Cl}$$

Magnetite Formation

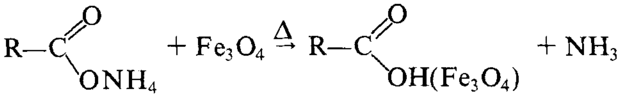
$$\mathrm{2FeO(OH) + Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O}$$

Saponification



$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7C({=}O)OH + NH_4OH \rightarrow R{-}C({=}O)ONH_4 + H_2O}$$

Peptization



$$\mathrm{R{-}C({=}O)ONH_4 + Fe_3O_4 \xrightarrow{\Delta} R{-}C({=}O)OH(Fe_3O_4) + NH_3}$$

Because of its use in densitometric concentrations, the apparent density of the FMF in a sufficiently diverging magnetic field is an important parameter. The following relations can be used as a guide to estimate some of these interrelated parameters.

$$T_S = 1.16 \times 10^{-4}\ C_{\mathrm{Fe}} - 1.70 \times 10^{-3} \quad (\pm 15\%)$$
$$T_S = 7.2 \times 10^{-2}\ P_A - 9.14 \times 10^{-3} \quad (\pm 1.5\%)$$
$$0.005 \leq T_S \leq 0.050, \qquad 1.5 \leq P_A \leq 8, \qquad 0 \leq C_{\mathrm{Fe}} \leq 500$$

where T_S = saturation magnetization of the FMF, Tesla, T
C_{Fe} = total Fe concentration in FMF, g Fe/L
P_A = apparent density of the FMF, g/mL

These relations have been obtained from actual data points and are valid to the degree indicated in the range of the variables indicated.

B. Equipment and Operation

1. Reactor and Settling Tanks (Fig. 1)

The reactor tank and settling tank are epoxy-coated aluminum vessels measuring 430 mm in height and 410 mm in diameter.

The reactor tank is externally heated by three electrical heating bands, spaced 25 mm apart, each band supplying 2.5 kW of power. Internally, the reactor tank has baffles arranged at 90° intervals, each baffle being 40 mm wide. Mixing is accomplished by a centrally located shaft having a flat blade turbine at the bottom of the shaft and a marine propeller a short distance up on the shaft. Cooling is achieved by a titanium tube cooling coil located inside the vessel. Both vessels have bottom discharge valves for FMF, by-product, and cleaning water discharge. The holding capacity of both vessels is about 50 L.

2. Dissolving and Mixing Tanks (Fig. 2)

The dissolving tank is a 38-L polypropylene cylindrical tank, with conical bottom, measuring 540 mm in height and 340 mm in diameter. Solid iron salts are dissolved by mixing with an eccentric shaft having two marine propellers.

The mixing tank is a 20-L polypropylene cylindrical tank measuring 370 mm in height and 280 mm in diameter. It is used primarily for mixing the kerosene–oleic acid mixture.

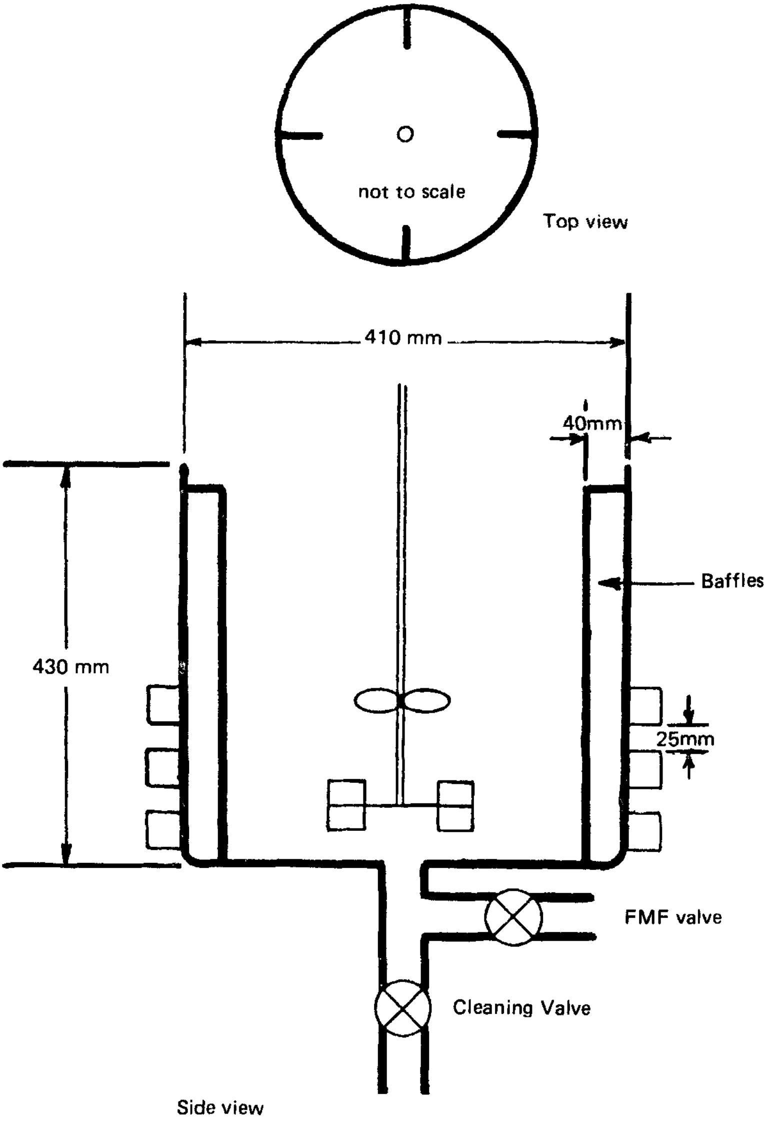


FIG. 1. Reactor tank.

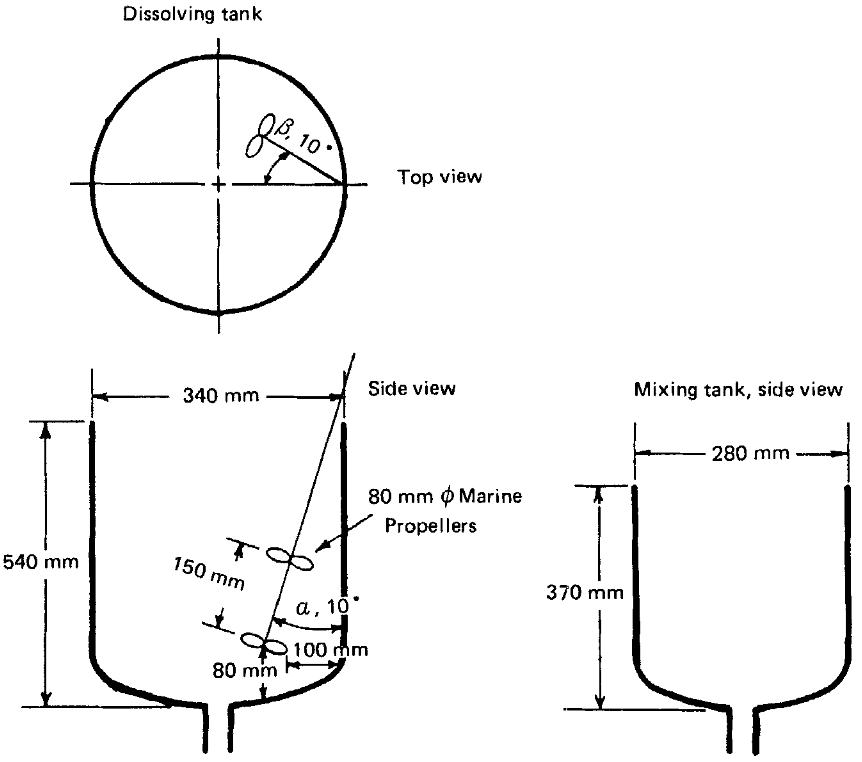


FIG. 2. Dissolving and mixing tanks.

3. Pressurized Ammonium Hydroxide Delivery System (Fig. 3)

The principal component in the pressurized ammonium hydroxide delivery system is a stainless steel pressure vessel having a calibrated sight gauge with charge and discharge openings.

Additional equipment includes a pump, a timer, a vacuum breaker valve, two two-way solenoid valves, and one three-way solenoid valve. Electricity and compressed air are the required utilities.

The system operates as follows: To fill with the required amount of ammonium hydroxide, solenoid valve B (SV-B) is deenergized (normally closed, NC) and SV-C is open (normally open, NO) in the 1-2 direction.

By turning on the pump, SV-A (NC) is energized, delivering ammonium hydroxide to the pressure vessel. As the pressure vessel is filled to the required level, air is displaced through valve SV-C in direction 1-2, while at the same time the vacuum breaker valve on the ammonium hydroxide drum admits air equal to the volume of liquid displaced. This is a quality control measure to prevent ammonia outgassing from the solution, thus lowering the concentration.

When the required amount of ammonium hydroxide is delivered, the pump is stopped, thereby closing SV-A.

To deliver the required amount of ammonium hydroxide, the timer is set for operation and SV-C is energized, changing the flow path to 3-1, thus admitting compressed air to pressurize the system. At the elapsed time, SVB is energized also, thus beginning delivery of ammonium hydroxide to the reactor tank. At the completion, all liquid has been delivered and the timer is deenergized, returning SV-B and SV-C to refill position. The remaining air pressure in the container is vented through path 1–2 of SV-C. The system now is ready to be filled up for another delivery.

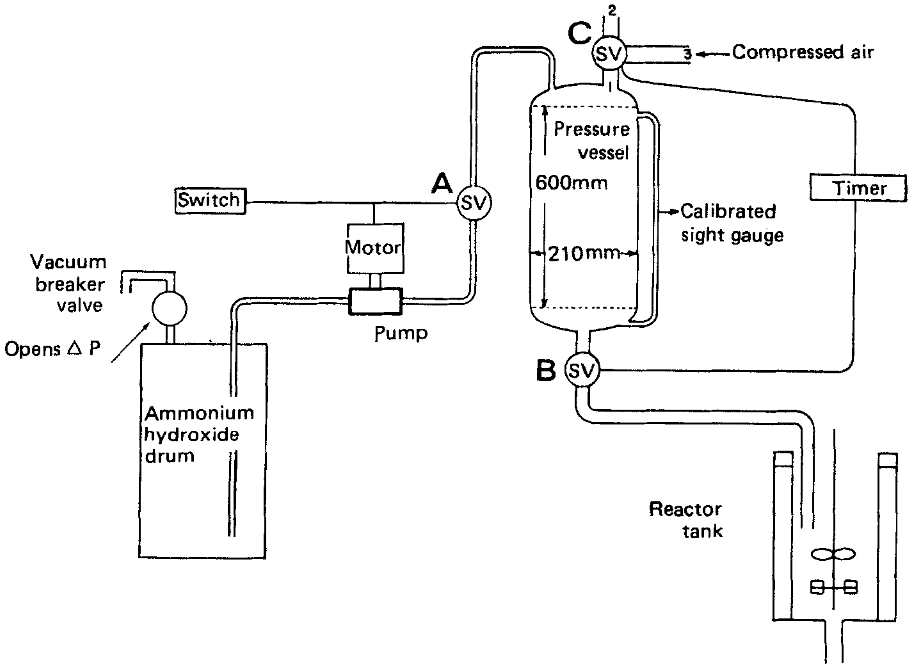
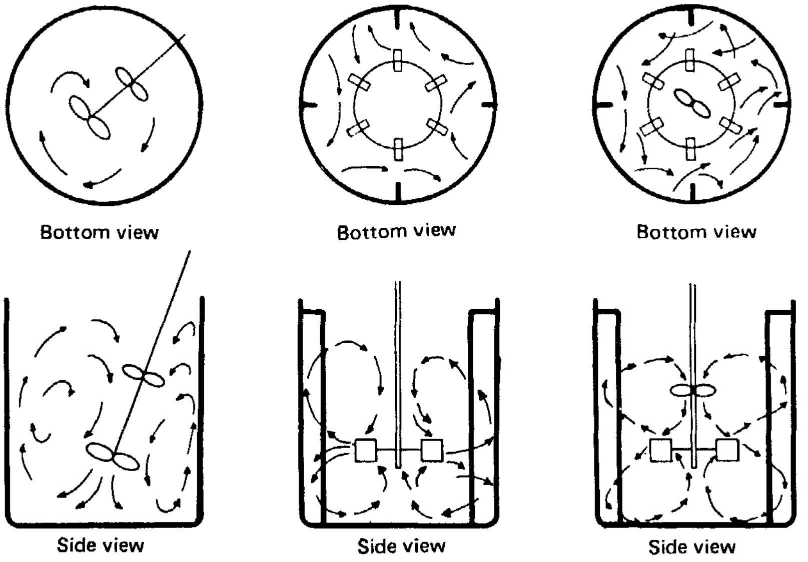


FIG. 3. Pressurized ammonium hydroxide delivery system.



Dual marine propeller

6-Bladed flat blade turbine
Bottom view

Single marine propeller
6-bladed flat blade
turbine

FIG. 4. Mixing patterns of various combinations.

4. Mixers and Related Equipment (Figs. 4 and 5)

All mixing motors are air turbines. Safety considerations suggested an air-operated motor whereas mixing conditions required constant torque at various speeds. The mixing shaft is 12.5 mm diameter, having two mixing blades on it. The lower one at the end of the shaft is a 100-mm diameter, 6-bladed, flat blade turbine whereas the upper one, 140 mm up on the shaft, is an 80-mm diameter, 3-bladed marine propeller with pitch equal to diameter. This combination of blades is particularly useful for intense mixing and dispersion as required for FMF manufacturing. Figure 4 shows the mixing patterns of the propeller and turbine individually and when they are combined in a single unit as in the process. Figure 5 shows the complete reactor tank assembly and the double 8 loop intense mixing pattern which is the pattern used for FMF manufacturing.

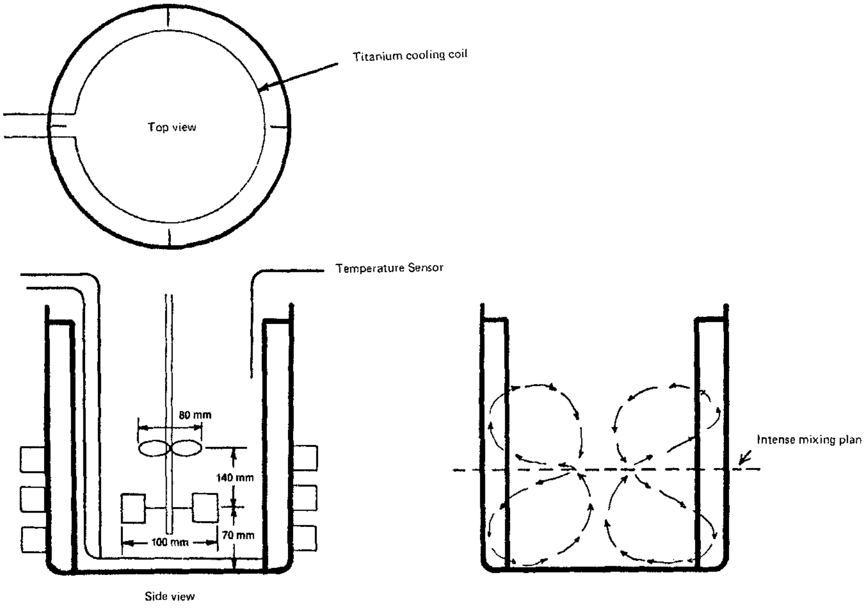


FIG. 5. Complete reactor tank assembly showing the "double 8 loop" and the intense mixing plane.

5. Temperature Control Unit and Fail-Safe Electrical and Cooling Systems (Fig. 6)

The reactor vessels are heated with three electrically powered heating bands spaced 25 mm apart starting from the bottom of the reactor. Each band is rated at 2.5 kW for a total input of 7.5 kW for the reactor. Power is supplied by a 3ϕ, 230 VAC circuit. Temperature control is achieved by a thermistor probe, signal amplication, and control relays in conjunction with cooling coils. The heating system also encorporates a fail–safe device. Should there be an incident (fire or other) where the chemical reactions are not under control, a panic button located at the other end of the pilot plant is activated. This action turns off power to the heaters and opens the cooling water solenoid valves so that the reactor contents are cooled automatically.

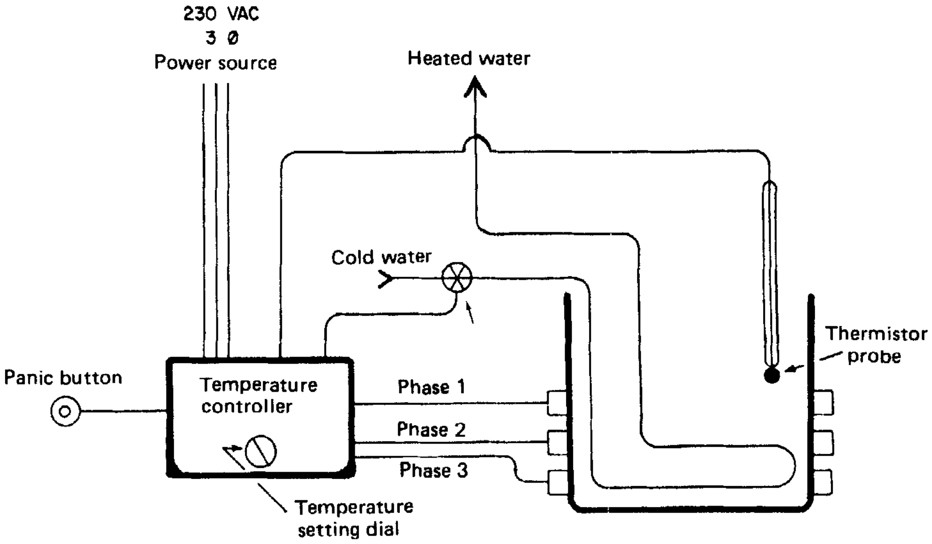


FIG. 6. Temperature control unit and fail-save electrical and cooling systems.

C. Raw Materials

Chemically pure raw materials are used. They are: ferric chloride, ferrous chloride, ammonium hydroxide, kerosene, oleic acid, and water. The high price of the iron salts prompted investigation of less expensive raw materials. Spent hydrochloric acid pickle liquor, spent sulfuric acid pickle liquor, and sulfate salts, rather than chlorides, have been investigated.

Spent hydrochloric acid from steel mill pickling operations is available as an inexpensive mixed ferrous–ferric chloride solution. Spent sulfuric acid pickle liquor is scarcer since steel mills have switched to hydrochloric acid pickling in the United States. Solid sulfate salts are available mainly from water treating sources; however, it has been found that the least expensive source of iron is the spent hydrochloric acid pickle liquor.

D. Manufacturing Procedure (Fig. 7)

The process is shown schematically in Fig. 7. The manufacturing rate is 30 L/7 h of FMF having a minimum saturation magnetization of 0.035 T. Subsequent dilution yields 52 L of 0.020 T FMF.

1. Dissolution

An FMF batch is begun by crushing solid ferric chloride to the suitable particle size range so that acceptable dissolution rates are obtained. To dissolve ferric chloride, high agitation rates in the order of 1300–1400 rpm are used. When dissolving ferrous chloride, agitation rates of about 650–750 rpm are used so as to minimize ferrous ion oxidation to ferric by the entrapped air.

2. Neutralization

Upon completion of the dissolution, the iron salts solution is pumped to the reactor vessel. Quality control is exercised on the iron salts solution and the ammonium hydroxide solution by measuring density and pH. At this time the reactor temperature is about 20°C. The ammonium hydroxide delivery system is filled and pressurized. The iron salts solution is neutralized by fast (20 s) ammonium hydroxide addition at 900 rpm agitation. During

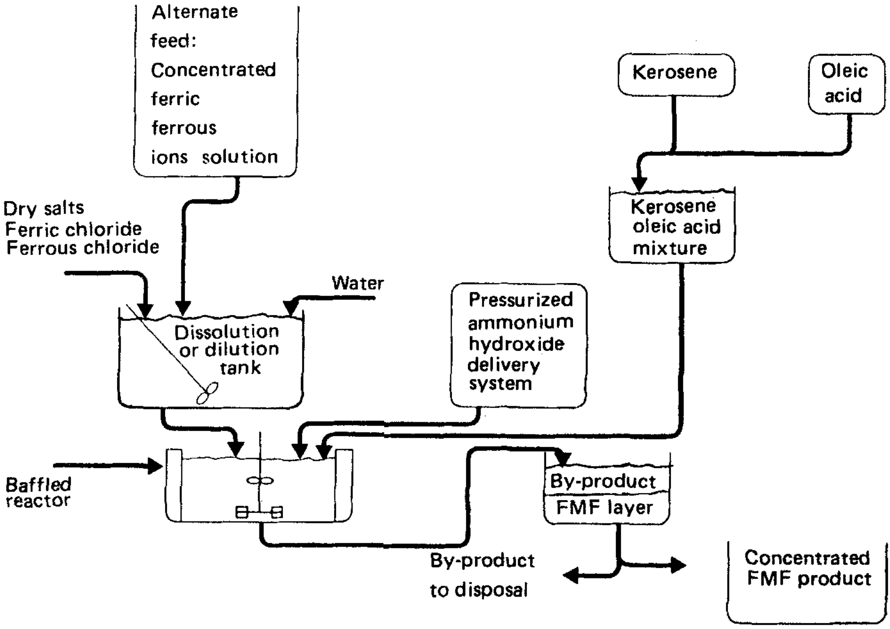


FIG. 7. FMF manufacturing process.

neutralization, the iron salts solution changes from rust color to deep brown while at the same time increasing viscosity until it is paste-like. Upon addition of an excess amount of ammonium hydroxide, the neutralized solution turns carbon black and its viscosity decreases to a watery consistency. During this time, magnetite is precipitated. At this point the pH and the temperature of the neutralized solution are noted, while 900 rpm agitation is continued for about 1 min.

3. Peptization (3)

The premixed kerosene–oleic acid mixture is gravity fed to the reactor while agitating its contents at 300 rpm. The heaters are energized and it takes about 45 min to reach 90°C, at which temperature the entire mass is held for 30 min.

During heating, the excess ammonium hydroxide reacts with the oleic acid to form an ammonium oleate soap soluble in water. At 90°C the ammonium oleate decomposes into oleic acid (which coats the magnetite particles) and gaseous ammonia. Since the oleic acid is mostly soluble in the kerosene phase, the coated magnetite particles are transferred there, while the gaseous ammonia evaporates. These reactions conclude the peptization process.

4. Product Recovery

At the end of 30 min at 90°C, the mixing is stopped and the reactor contents are cooled to about 75°C. This is a safety measure taken so that the contents do not exceed 85°C during phase separation. The reason for keeping the mixture at 75–85°C is that phase separation is faster at higher temperatures while, at the same time, the temperature is not high enough for boiling and, therefore, remixing.

Most of the product is separated during a 20–30 min period after which it is transferred by decantation to a settling vessel where the residual aqueous phase of ammonium chloride separates out. If large quantities are generated, the solution may be sold to zinc–carbon battery manufacturers or some other outlet.

5. FMF Quality

Batch success is measured by the amount of fluid obtained and by the pH of the by-product, ammonium chloride. FMF quality is measured by the saturation magnetization of the fluid with a digital readout equipped electronic magnetization saturation meter which was specially custom constructed and used as the quality control instrument (*4*).

6. *The Effect of Mixing*

It has been established that for good quality FMF, a standardized mixing procedure must be followed. Fast mixing is required during neutralization in order to disperse the ingredients and to prevent magnetite crystal growth. Slow mixing is ineffective and yields poor quality product, small in amount, and of low saturation magnetization. On the other hand, slow mixing is required during the peptization step in order to prevent adverse emulsion formation. Fast mixing at this stage yields mostly adverse emulsion which is difficult to break up.

7. *The Effect of NH_4OH Addition Rate*

A fast ammonium hydroxide addition rate, 0.46 L/s, has been established to be optimum for the pilot-plant scale operation. A slow addition rate, 0.0167 L/s, results in emulsion formation since the slower neutralization rate promotes adverse side reactions. Not all iron is precipitated as magnitite, and a large excess of ammonium hydroxide is available which would emulsify some of the kerosene.

Thus magnetite precipitation is a rate-dependent process. Similarly, an excess of ammonium hydroxide added at the correct addition rate results in adverse emulsion formation; however, whatever amount of FMF is made, is concentrated.

8. *The Effect of the Purity of Chemicals*

As mentioned in Section II-C, all the chemical materials used for feed are relatively pure. FMF has been manufactured from spent pickle liquors. It is well known that spent pickle liquor may contain small amounts of copper, zinc, cadmium, and other metals as well as about 1% hydrochloric acid. The effect of these impurities appears to be insignificant.

Ammonium hydroxide is widely available as a pure solution at relatively low prices. Therefore, no effort has been made to find a less expensive, impure solution.

III. PRODUCTION RATE AND COST

Kerosene is a mixture of aliphatic and aromatic hydrocarbons. Though the exact composition of a batch of kerosene can be obtained, it is rather meaningless because the ratio of the various hydrocarbons changes significantly from batch to batch. Nevertheless, the general composition of the chemical named kerosene remains the same. No unusual behavior has been observed with kerosene from a variety of sources.

The effect of the purity of oleic acid is believed to be insignificant since it has been reported by the USBM that FMF has been made with tall oil rather than oleic acid. Tall oil is a resinous by-product from the manufacture of chemical wood pulp. It is used in making soaps, coatings, and various oils. Thus, some cost reduction would be achieved if tall oil were less expensive and widely available.

1. Dilution of the Product to Required Concentration

Dilution to the required concentration is achieved by the conventional methods using mass balance equations. The diluent is the base carrier; for kerosene-base FMF, kerosene is used as diluent.

IV. PRODUCTION RATE AND COST

The pilot plant was set up to produce 2.15 L/h of 0.035 T FMF. After a few trial runs the process was improved and capacity was expanded to 4.30 L/h of 0.035 T FMF. On one occasion, 210 L of 0.040 T FMF were manufactured over a period of seven working days.

A substantial amount of manufacturing information was obtained which permitted calculation of the cost of FMF at the use and expanded capacity and is shown in Fig. 8.

The data were obtained by adding the cost of feed materials, labor and supervision, and utilities. Spent hydrochloric acid pickle liquor was considered as the source of iron ions. The mentioned cost components are also a function of time (5–7).

As the daily FMF production rate increases in an automated plant, the unit labor cost diminishes and the production cost/L for large volumes approaches the chemical cost. At a production rate of 575 L/7 h of 0.035 T FMF, which is subsequently diluted to produce 1000 L of 0.020 T FMF, the cost of the 0.020 T FMF would be less than $1.00/L. Published opinion

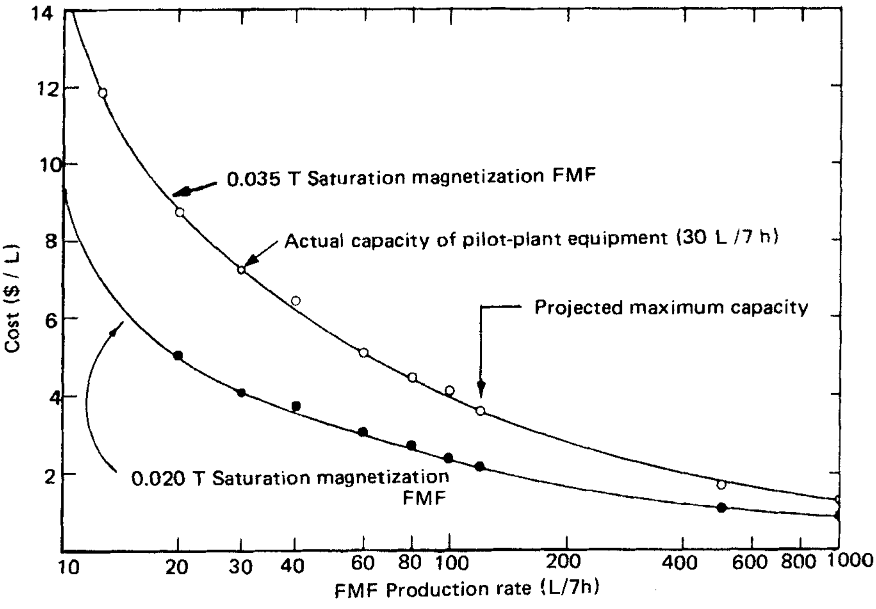


FIG. 8. Effect of production rates on FMF unit cost. Source of iron, spent pickle liquor.

cites FMF as being economically attractive for densitometric concentrations if the price is around $1.00/L for the 0.020 T Fluid (*8*).

Further price reductions would be possible by using sulfate solutions instead of the chloride derived from spent pickle liquor. The capital investment in a full-size plant handling sulfates should be less than in a plant handling chlorides because sulfates are less corrosive, thereby allowing less expensive equipment to be used. The operating cost of a plant using sulfates should also be less than that of a plant using chlorides because sulfates are less costly than chlorides. Thus, specific costs should be obtained for each case considered.

V. CONCLUSIONS

A pilot-plant manufacturing process for kerosene-based FMF has been described. It consists of a modified version of the USBM developed peptization process.

An integrated version of the process has been successfully run at the 30 L/7 h rate which produced a nominal FMF concentration of 0.035 T. Expansion of this capacity by increasing processing volumes throughout and automation would decrease the unit costs sufficiently to make FMF economically attractive as a tuneable density concentration medium.

Acknowledgments

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