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Removal of Heavy Metal Ions by Superconducting Magnetic Separation

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ABSTRACT

Several industrial sectors such as surface treatment, petroleum, chemical, etc. generate effluents containing heavy metal ions (HMI). The main metal ions in such effluents can be zinc, copper, vanadium, etc. Purification of such effluents by magnetic separation is performed by adding a certain proportion of iron salts. These salts precipitates together with those of HMI by increasing the pH. The coprecipitation of this “magnetic carrier” with heavy metals hydroxydes to create a magnetic floc has been studied. The effluent treated passes by a superconducting separator where the flocs are retained in a matrix of steel wires. The purified effluent leaves the separator, and the trapped flocs are collected when the matrix is saturated. The efficiency of HMI separation by this method exceeds 95%.

INTRODUCTION

In mineral processing, conventional magnetic separators are equipped with traditional magnetic circuits. Superconducting magnet technology allows fields to be generated that are significantly higher than those generated by either conventional electromagnets or permanent magnet technology. The results obtained by superconducting separation of industrial minerals show that it is possible to attain a degree of purification better than that of traditional

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magnetic separation (1, 2). Mining and metallurgical operations handle large volumes of process water which are contaminated with fines, metal ions, oils, and other undesirable materials. Aqueous streams containing heavy metals are frequently encountered in industrial effluents. Ni, Cu, Zn, Cd, etc. are very common in electrolytic refining plants, surface treatment shops, and in acidic mine water. It is also possible to use a cryomagnetic system to remove the metal ions contained in process water following a precipitation phase with iron salts.

Recent advances in magnetic separation science have resulted in the successful development of high-intensity, high-gradient, and cryogenic superconducting separators capable of dealing effectively with a broad range of separation problems that have appeared insoluble in the past.

For instance, the new generation of separators can separate weakly paramagnetic materials even at small size distribution, while the new technology of magnetic filtration has succeeded in removing submicron particles in wastewater treatment (3).

For many years the conventional method for heavy metal removal has been precipitation–settling of metal hydroxides followed by thickening and/or filtration of the sludge. For example, most dissolved metal ions contained in urban or industrial wastes are treated by this process (4, 5).

PARTICLE RETENTION IN A MAGNETIC FILTRATION SYSTEM

The principle of strong-field/high-gradient magnetic separation consists in producing strong heterogeneities in an originally homogeneous outside magnetic field by using small ferromagnetic elements. This results in the creation of force centers with a small range on which any paramagnetic substance will be trapped (6, 7).

The method is based on the use of magnetic-attraction forces which retain paramagnetic particles in a solid/water suspension on magnetized matrix elements (Figs. 1 and 2). Both particles with a nonsufficiently high magnetic susceptibility and nonmagnetic particles, i.e., the cleaned product, will flow out of the system. Figure 1 shows how the solid/water suspension flows through a matrix, whose elements, when exposed to a magnetic field, develop high field gradients immediately around the wires. In mineral processing, when the retention capacity of the matrix has been reached, suspension feed-flow is stopped and the matrix, still under a magnetic field, is flushed with clean water to eliminate mixed or mechanically trapped articles. After this, the field is switched off and the magnetic particles are removed with a high-pressure water jet (Fig. 2). In environmental processing the magnetic field is maintained and the magnetic particles are eliminated from the matrix by their dissolution by acidic solution.

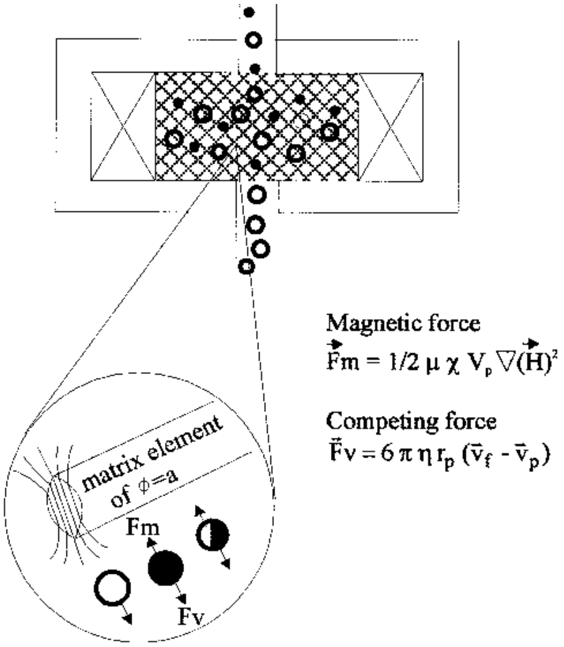
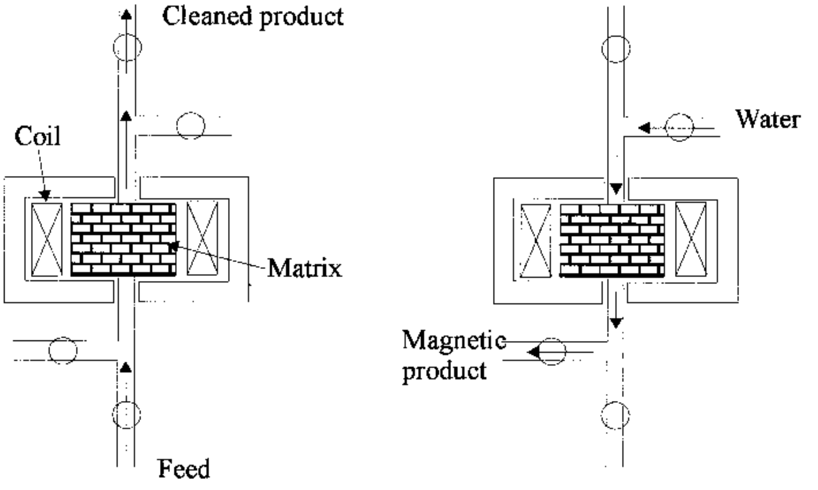


FIG. 1 Cross section of a filter and attraction to a magnetized wire.



A - Feed in a magnetic field

B - Recovery of magnetic product (no magnetic field)

FIG. 2 Operating principle of a high gradient filter.

Magnetic separation is achieved by a combination of a magnetic field and a field gradient which generates a force on magnetizable particles such that paramagnetic and ferromagnetic particles move toward the higher magnetic field regions and the diamagnetic field particles move toward the lower field regions (7). The force F_m on a particle is given by:

$$F_m = \frac{1}{2}\,\mu_0\,\chi\,V_p\,\nabla\,(H^2), \qquad \text{with } \chi = \chi_p - \chi_f$$

where χ_p and χ_f are the magnetic susceptibilities of the particle with volume V_p and the fluid, $\nabla(H^2) = \text{grad}(H^2)$ represents the magnetic field and the magnetic field gradient, where ∇ represent the gradient operator, and μ_0 is the constant $4\pi \times 10^{-7}\ H/\text{m}$ (vacuum permeability).

The fundamental element in the capture process is the interaction between a small magnetizable particle of radius r_p, usually paramagnetic, in a uniformly applied magnetic field. In a high gradient filtration system, we consider a ferromagnetic wire of radius a and a saturation magnetization M_s (Fig. 1). A uniform field H large enough to saturate the wire is applied. Paramagnetic particles of susceptibility χ_p and volume $V_p = \frac{4}{3}\,\pi r_p^3$ and density p_p are carried past the wire by a fluid of viscosity η moving with a uniform velocity V_f.

The flow around the wire is treated in the hydrodynamic approximation in which the fluid can be considered frictionless. The equations of motion can be derived by settling the Stokes viscous drag F_v and the gravitational force F_g on the particle to the magnetic force F_m.

$$F_v = 6\pi\eta r_p(V_f - V_p)$$

where V_p is the particle velocity.

$$F_g = \frac{4}{3}\pi r_p^3(p_p - p_f)\ \text{g}$$

where p_p and p_f are the specific gravities of the particle and the fluid.

The equation of motion is obtained from $F_m + F_v + F_g = 0$, and to have an effective separation it will be necessary to respect the relation

$$F_m > F_g + F_v$$

EXPERIMENTAL

Equipment Used (Fig. 3)

The developed system (8) is composed of three parts: the magnet, the cryogenic system, and the control unit.

The Magnet

The superconducting solenoid winding is constituted by a Nb-Ti monolithic multistrand conductor. The magnetic field obtained is 5 T on the solenoid axis

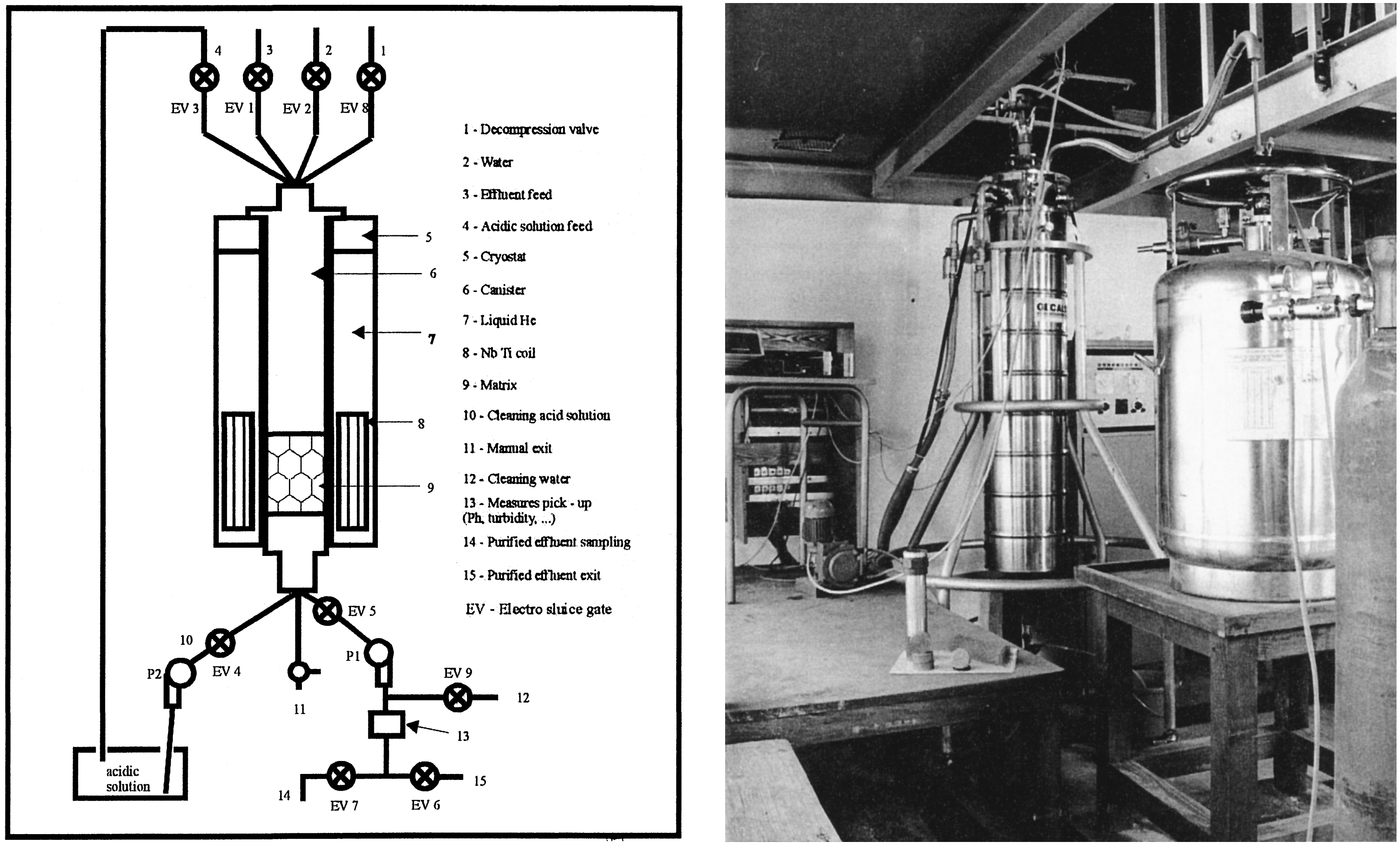


FIG. 3 Superconducting magnetic separator and flow sheet of metal removal.

with a leakage field, at 1.5 m, of about 8×10^{-4} T. The stainless steel cryostat is coated by superinsulation and has thermal shields cooled by helium gas. The cryostat has a central hole of 120 mm diameter. The matrix is in the canister and is located in the magnetic active part created by the solenoid (350 mm). The magnetic field can be controlled either manually or automatically.

Cryogenic System

This cryomagnetic unit differs from most similar systems in that it requires no external liquid helium supply. It has its own integral helium liquefier and a fully closed helium circuit. The main components of the circuit are:

A *liquefier* including:

- A cryogenerator.
- Three heat exchangers with a Joule–Thomson pressure reduction system.
- Two shields at 15K and 80K cooled by the cryostat evaporation gases.

A *compressor*: It is a lubricated screw type which is fed by the gases coming from the cryostat.
A *vacuum chamber*, a ballast tank (He).

The system described satisfies the essential conditions for reliability:

- Good helium quality in the closed circuit is ensured by charging with very high purity gas and by the purification system included.
- Service intervals for the cryogenerator and compressor are about 8000 hours.

In the operation of industrial effluent purification, the separation cycle system as described above is not necessary, and thus the cryogenic system does not require a switched mode system. In this case the superconducting magnet can be operated in a persistent mode which simplifies the technology of the superconducting magnet of the associated cryogeny.

A further important feature of this cryosystem is that when the superconducting magnet operates in a persistent mode, it is possible that the magnet can be completely isolated from external power requirements once it is energized.

Programmable Control Unit (8, 9)

The operation and maintenance of such a system can be simplified by extensive automation, thus minimizing manual intervention. This has been achieved by means of a versatile programmable control unit which performs all operations required for the establishment of the operating conditions (cryogenics); setting up, control and shutdown of the magnetic field, etc.

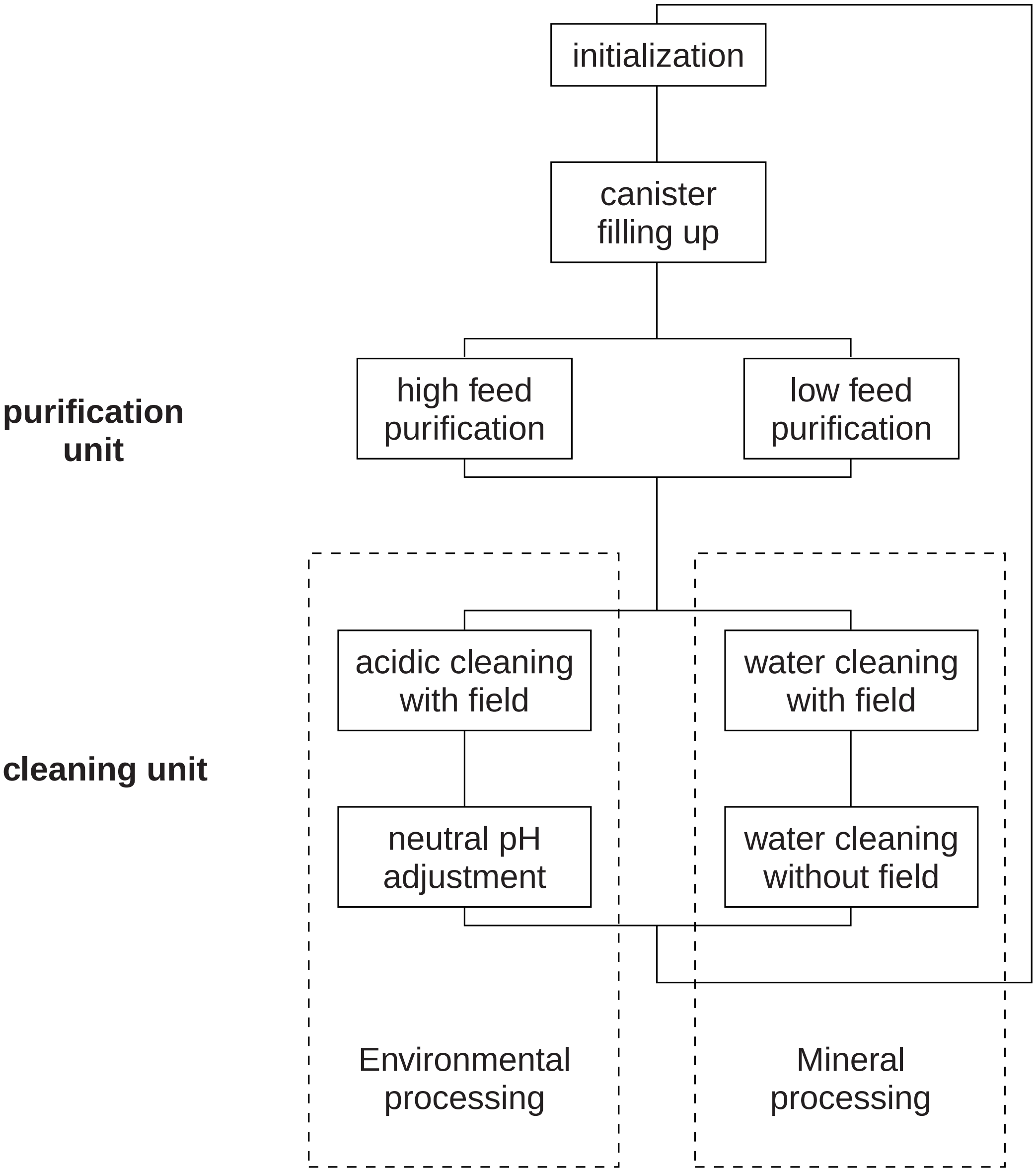


FIG. 4 Principle and automation diagram of separation cycles.

The control unit can be programmed for the different separation cycles (mineral or environmental processing) as shown by Fig. 4. The mineral processing protocol can be adapted for effluent purification by modifying the matrix rinsing system. This has been performed by using GraphCET instructions because they give good flexibility.

The GraphCET design employed in this study is more elaborate than the conventional industrial ones because all the separation parameters (feed system, rinsing water or acid solution of the matrix, products recovery, sampling field command, etc.) are programmed. The automation must be modulable capable of reacting to different instructions or complementary apparatus. We chose Toshiba EX 100 as the automation control because it is modulary and enables rapid adaptation to the equipment necessary for process control. The dialogue between the user and Toshiba EX 100 for defining the process parameters was made by a Quick Control LTD model QI 10. Programmation of those two systems was executed by a PC computer.

Testworks Procedure

A specific installation was designed as part of this R&D effort for the processing of effluents through extraction of precipitated and coprecipitated metals as magnetic “flocs,” i.e., magnetic metal hydroxides and coprecipitated magnetic and/or nonmagnetic metal hydroxides (10, 11). Removal of flocs from the matrix is obtained by a simple chemical modification caused by rinsing the matrix with an acidic solution (Fig. 3) rather than by switching off the magnetic field. The acidic solution is charged with metals trapped in the matrix after the feed flow is stopped.

The solution, whose volume is limited to that of the canister, can be recirculated for progressive charging with metals and until sufficient metals are contained for electrolytic processing.

This process presents several advantages over the “standard” system:

- A smaller volume of waste is produced, which facilitates handling and later treatment.
- The magnetic field no longer needs to be switched off, which makes the coil technology simpler and reduces the operating cost because less helium is used (12).

Search for a Magnetic Carrier for Dissolved Metals (10, 11)

An interesting way to create a magnetic support is through coprecipitation of the element to be eliminated with a hydrous iron oxide. The latter should have sufficient magnetic properties for magnetic separation to be efficient.

A major effort was made during the work on this project to define such hydrous oxides and to understand their behavior. Various modes of metal adsorption on hydrous iron oxides were studied. Figure 5 shows a mixture of ferric chloride and ferrous sulfate in a ratio of 1 mole of ferrous iron to 2 moles of ferric iron (“Fe_3O_4” solution). This led to the precipitation of a hydroxide with strong magnetic properties.

This ratio corresponds to that of magnetite, Fe_3O_4, but, depending on the amount of iron in solution, the precipitate as identified by XRF analysis could be either magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3). The latter precipitates

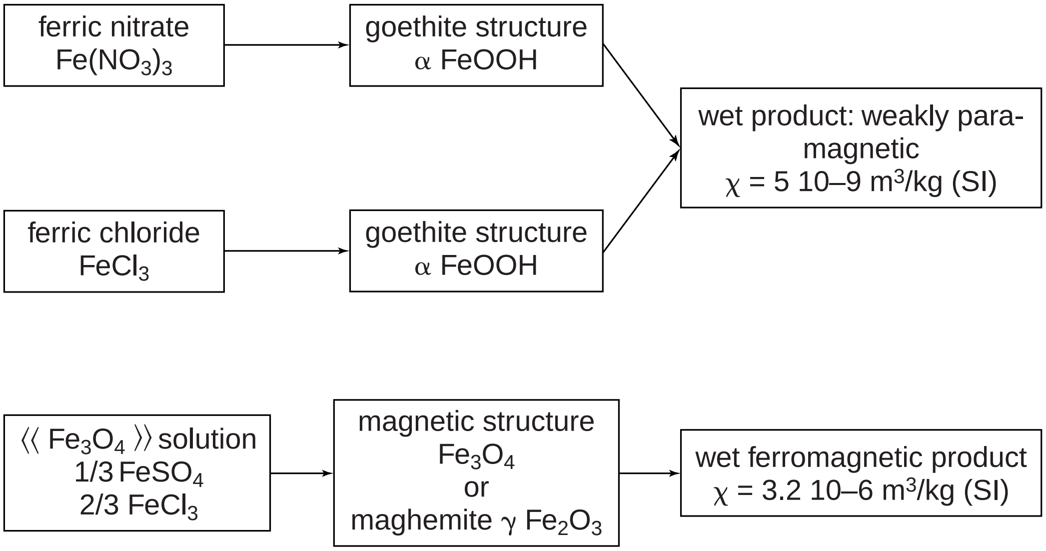


FIG. 5 Different iron-salt precipitates.

from a solution containing less iron. Maghemite is the unstable phase of hematite (α-Fe_2O_3), with a spinel structure that shows a magnetite (Fe_3O_4) spectrum upon drying.

Depending on the concentration of iron in the solution, the nature of the precipitate will change, but there is also a threshold value beyond which the precipitate will no longer have interesting magnetic characteristics. This boundary concentration of iron will vary according to the type and concentration of the metals dissolved in the fluid to be cleaned because those metals "dilute" the magnetic susceptibility of the end product. Grain size measurements were made on precipitates from only the "Fe_3O_4" solution.

A "Fe_3O_4" solution precipitated at 5 mmol of total Fe shows a d_{50} of almost 15 µm whereas a more concentrated solution at 7.5 mmol gives a d_{50} of 2.4 µm. Below 7.5 mmol/L of iron, the precipitate will be a strongly hydrated floculate with a structure close to that of goethite, as in the case of ferric chloride (10, 11).

Therefore a mixed solution of ferrous and ferric salts (the latter forming the "magnetic carrier") was added to the waste to be processed. Precipitation was obtained by raising the pH of the solution. The hydrated magnetite obtained traps the metal ions to be eliminated by adsorption and or coprecipitation. Magnetic filtration allows this precipitate to be retained in the matrix.

The purified effluent can be expelled directly to the natural environment or, when the matrix is saturated, the precipitates can be dissolved with a circulating acidic solution. This concentrated solution can be recycled several times. This flushing operation is performed without a magnetic field, thus allowing

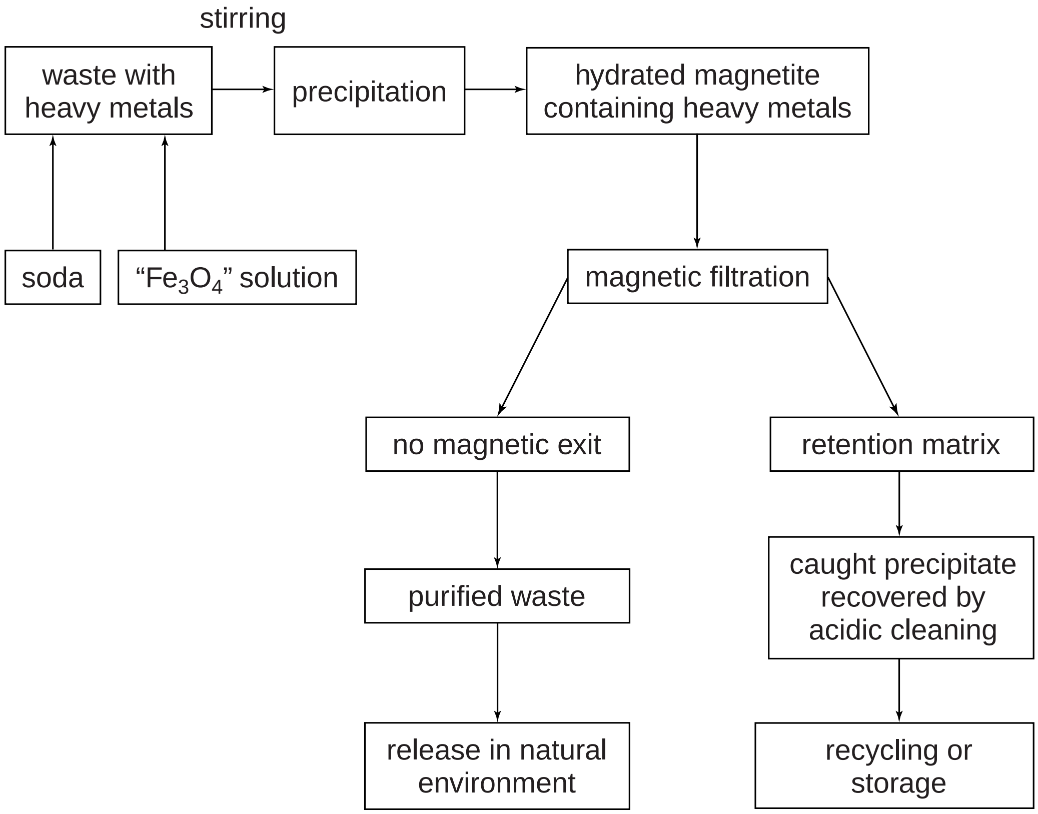


FIG. 6 Experimental procedure.

a considerable saving of time, energy, and helium consumption. This process is shown in Fig. 6.

Experimental Separation Tests Procedure (10, 11)

Several tests were made with synthetic materials with the test procedure shown in Fig. 6. As an example, Table 1 shows the results obtained on a product containing five metals in solution: 20 ppm of Cr and 10 ppm each of Ni, Cu, Fe, and Zn. We tested the influence of the proportion of "Fe_3O_4" solution added to the solution containing the metals. To be safe, the pH of the solution was stabilized at 12 by adding NaOH. Table 2 gives the concentration of metals to be eliminated and the concentration of Fe added.

By simple precipitation of the solution without the addition of Fe, the purification percentage for each of the metals is only 40% for one passage. Recycling the prepurified solution in the separator does not improve this result; everything that could be magnetically trapped was retained during the first passage. It should be noted, however, that nonmagnetic metals such as zinc or copper are retained in the same manner on the flocs because of coagulation

TABLE 1
Magnetic Purification of a Polymetallic Synthetic Product

Mass ratio of Fe added	% of purified metal				
	Fe	Cr	Ni	Zn	Cu
0	37.0	37.0	45.0	32.0	42.0
12	79.3	58.5	88.1	31.5	75.9
31	97.4	96.6	>99	86.3	>99
45	99.1	>99	>99	83.3	>99

and adsorption phenomena. Iron and chromium, however, which have the same purification percentage of 37%, probably precipitate together by substitution of the chromium in ferric hydroxide sites. Above a weighted ratio of 30 for the total iron added to the metals, all metals except zinc are retained in the separator during a single passage.

The purification of zinc appears to be more complex. Because of the amphoteric character of zinc precipitates, both trapping by ferriferrous flocs and/or coprecipitation are strongly reduced when the ratio of total Fe to metals is low.

SEPARATION RESULTS ON INDUSTRIAL EFFLUENTS (10, 11)

The treatment of industrial effluents was also studied. Such fluids mostly come from surface treatment with rinse water. The main metal in such effluents may be zinc or copper, depending on the source. Fluids from the rinsing of used vanadium-based petroleum were tested as well.

These different rinse waters have relatively low concentrations (20–30 mg/L) of the main dissolved metals, but they can contain smaller amounts of other dissolved metals. The latter are not commonly quantified in the data pro-

TABLE 2
Concentration of Metals to Be Eliminated and Concentration of Fe Added

	Samples			
Samples	1	2	3	4
Fe added (mg/L)	0	670	1675	271.8
Metals to be eliminated (mg/L)	60	57.6	54	48
Mass ratio of Fe/metals	0	12	31	45

TABLE 3
Purification Results for Industrial Rinsing Fluids

Main metal (M) in the fluid (mg/L)	Concentration before treatment		Residual concentration after treatment		% Purification	
	M (mg/L)	Added Fe (mg/L)	M (mg/L)	Added Fe (mg/L)	M (%)	Added Fe (%)
Cu[a]	21.29	705.8	0.04	9.19	99.81	98.7
Zn[b]	18.57	473.2	0.05	1.81	99.73	99.62
V[b]	38.60	720.3	[c]	5.7	100	99.21

[a] Reconstituted according to industrial effluent's composition.
[b] Industrial effluent.
[c] Less than determination limits.

vided by industry because they are considered to be secondary. Moreover, such rinse waters may contain reagents, in particular foaming agents, that were necessary for earlier steps in the industrial process. Each fluid must be subjected to preliminary tests in order to determine the amounts of iron that must be added to obtain a generally magnetic product because other impurities that can be precipitated in addition to the dissolved metals will be trapped in the flocs as well. Table 3 shows the purification performance obtained for each case.

To determine the volume of effluent to be purified during a cycle, tests were performed using the industrial copper and zinc effluents described in Table 3. A copper sample was reconstituted in laboratory based to the industrial effluent's composition.

"Fe_3O_4" solution was added in excess to the three effluents described in Table 3 in order to obtain magnetic precipitates. The cations contained in the three samples were precipitated at pH 9–9.5, and the precipitate had high paramagnetic susceptibility. The precipitated effluent was fed to the separator while using the maximum magnetic field of 5 T (4000 kA/m)* at a flow rate of 10 L/min for the copper sample and 12 L/min for the zinc sample.

The matrix was a stainless steel "knit mesh" of 0.11 m diameter and 0.35 m length.

Figure 7 shows the evolution of magnetic purification as a function of the treated volume of each sample.

Magnetic purification is complete for each effluent for a specific number of treated liters. When this volume is exceeded, effluent purification decreases

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* In SI units, 1 T = 800 kA/m.

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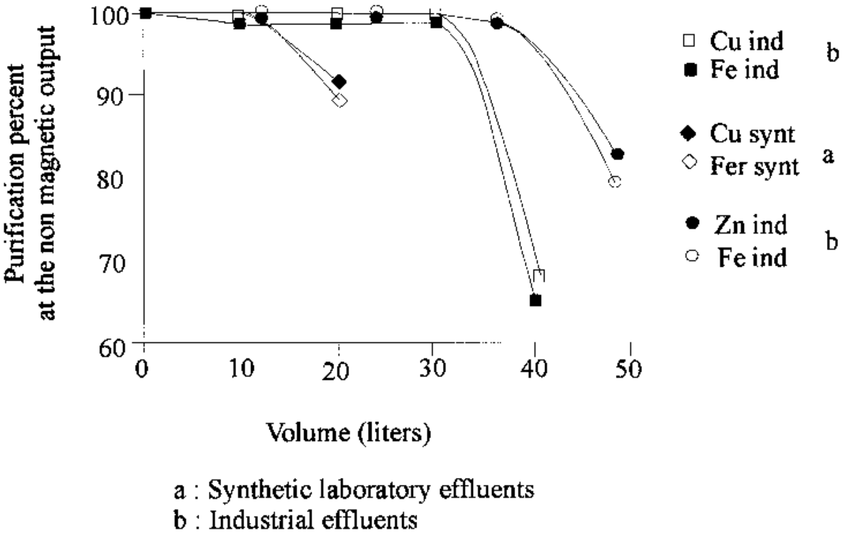

FIG. 7 Magnetic purification of Zn and Cu samples.

sharply. This degradation corresponds to matrix saturation by the precipitate. In such a case it is necessary to interrupt the feeding and clean the matrix.

The zinc sample yields the most important purified volume (35 L). The quantity purified is proportional to the volume of precipitates generated by the addition of the iron compound. This is confirmed by the feeble ratio of this effluent as shown in Table 4.

For an industrial type of processing with a retention matrix 0.5 m high with a 1 m^2 area, for example, the purified output of the zinc bath is 100 $m^3/h/m^2$. This output corresponds to that found in the purification of kaolin and enables use of a magnetic separator with its normal feeding regime (10, 11).

TABLE 4
Characteristics of the Copper and Zinc Baths before Treatment

	Concentration of metal M		Concentration in Fe added		Ratio Fe/metal	
Product	mg/L	mmol/L	mg/L	mmol/L	Weight	Molar
Cu[b]	21.29	0.33	705.8	12.6	33.15	38.2
Cu[a]	14.57	0.23	728.3	13	50	56.5
Zn[b]	18.57	0.28	473.2	8.47	25.5	30.2

[a] Reconstituted according to industrial effluent's composition.
[b] Industrial effluent.

CONCLUSION

This research confirms the usefulness of cryomagnetic separation as it applies to nonferrous waste materials, and it aids in understanding the technical difficulties of implementing this technique.

This paper presents and describes a separator with the following characteristics: integrated liquefaction unit, entirely closed helium circuit, self-contained system for about 8000 hours, and a magnetic field of 5 T.

The system's operation and maintenance is simplified by extensive automation realized through a versatile programmable control unit.

The range of applications of such an installation includes the extraction of metals from fluids that have to be processed before being discharged into nature because of the evermore stringent regulations governing such discharges and the absence of really viable alternative methods for removing very small amounts of metal. The standard methods for removing metals involve massive precipitation, implying the disposal of large amounts of sludge, which is rapidly becoming a problem in its own right.

The process defined in this paper (12) treats important volumes of industrial effluents charged with metals in solution without adding solid or coagulant salt, but does use a mixture of ferric chloride and ferrous sulfate. This technique is of common interest for the processing of fluids charged with small amounts of dissolved metals which are difficult to treat with conventional precipitation and thickening. The flocs recovered in acid solution present an important reconcentration of metals that make further treatment or recycling possible.

Magnetic separators powered by low temperature superconductors of the niobium type have been used to improve the brightness of kaolin clay for twenty years. The main disadvantage of these superconducting magnets is the need to cool the coil to 4 K, the critical temperature (T_c) to which the coil must be cooled in order to maintain its superconducting properties (13).

Superconductors with a high critical temperature, which retain their superconducting properties up to 90 K (i.e., above the liquefaction temperature of nitrogen) were discovered nearly a decade ago. Significant progress has been made in the production of thin films and wires of high T_c superconductors such as YBCO (yttrium barium copper oxide). Advances have also been made in the production of bulk YBCO which behaves similarly to permanent magnets. The application of high T_c superconductors to magnetic separators for treating a variety of industrial products is likely to be realized in the coming decade.

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REFERENCES

1. J. H. P. Watson, "Status of Superconducting Magnetic Separation in the Mineral Industries," *Miner*. *Eng*., *7*(5–6), 737–746 (1994).
2. D. Richards, J. Boehm, and R. Allen, "Commercial Acceptance of Superconducting Magnetic Separation," in *Proceedings of the IMPC*, Aachen, 21–26 September 1997, pp. 639–648.
3. T. Okuda, I. Sugano, and T. Tsuii, "Removal of Heavy Metals from Wastewater by Ferrite Coprecipitation," *Filtr*. *Sep*., (12), 472 (1975).
4. J. H. P. Watson and D. C. Gilwood, "Biomagnetic Separation and Extraction Process for Heavy Metals from Solution," *Miner*. *Eng*., *7*(8), 1017–1028 (1994).
5. G. Gillet, V. Bureau, and R. Houot, "Application de la séparation magnétique á l'épuration des eaux urbaines et industrielles," *Mines Carriéres*, *Tech*., pp. 51–61 (1992).
6. J. Svoboda, "Magnetic Methods of the Treatment of Minerals Development," in *Mineral Processing*, Vol. 8, Elsevier, 1987.
7. G. Gillet, "Séparation magnétique," *Les Techniques de l'Ingénieur*, A5220, A5221, A5222 (total 32 pp.) (1991).
8. G. Gillet and F. Diot, "Evolution technologique dans le domaine du tri magnétique," *Mines Carrières*, *Tech*., *I*/*II*, 4–14 (1996).
9. G. Gillet, H. Vedrine, et al., *Cryomagnetic Separation of Nonferrous waste*, Final report EEC, 1994.
10. G. Gillet et al., "Epuration Cryomagnétique d'Effluents Liquides Industriels," in *Proceedings of the Colloque International de Recherche sur les Sous-Produits de Traitement et d'Epuration des Eaux*, Poitiers, France, September 29–30, 1994.
11. V. Bureau, "Adaptation de la séparation cryomagnétique aux technologies de l'environnement: application à l'épuration d'effluents liquides industriels," INPL Doctorate Thesis, 1993.
12. French Patent 9308000-30-06-93 (BRGM-INPL), "Procédé et dispositif d'extraction des métaux paramagnétiques."
13. J. Kopp, "Superconducting Magnetic Separators," *Magn*. *Electr*. *Sep*., *3*, 17–32 (1991).

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