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ADVANCE IN CRYOMAGNETÏC SEPARATION PROCESS: INDUSTRIAL MINERALS AND WASTE EFFLUENTS

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Abstract: The principle of magnetic separation described here is to treat the solution loaded with dissolved metals by adding a certain proportion of iron salt, which, as it precipitates, entrains and imprisons the metallic hydroxide. The fluid treated is sent to a superconducting separator where the floes are retained in a matrix of steel wires. The purified fluid leaves the separator, and the trapped solids are collected when the matrix is saturated.

Conventional mineral separation methods cannot be scaled up directly to fluid depollution to recover the floes. It was therefore necessary to develop a variant of these processes, and to automate for an industrial demonstration.

1 INTRODUCTION

The performance offered by high-field, high-gradient magnetic separation in the field of mineral purification has given rise to the application of this process for the purification of industrial waste, particularly from surface treatment facilities. High-gradient magnetic separation very often offers a solution to the problems of purifying urban and industrial wastewater. Two types of application are available: the removal of solid paramagnetic particles in suspension in the effluent treated, or the removal of dissolved or ultrafine elements by magnetic seeding and coagulation/flocculation.

Dissolved metals from industrial effluents are usually precipitated as hydroxides or sulfurs. The precipitate is then decanted and filtered with the final cake stored in basins or lagoons. Magnetic separation (or magnetic filtration) can be used to decrease the separation time between mud and liquid. The conventional method consists of doping the mud with magnetic seeds (fine magnetite or hematite) which are incorporated in the preexisting flocculates.

A magnetic carrier can also be generated by coprecipitation of the element to be removed with ferric chloride, ferric nitrate or with a mixture of Fe'VFe'^{11}.

2 PURIFICATION OF A FLUID LOADED WITH DISSOLVED METALS

This type of purification is carried out today by precipitating the metals in hydroxide form. After settling and mechanical filtration, the slurries are dried in basins and lagoons. Magnetic filtration considerably accelerates the process of slurry/liquid separation, and hence increases the throughputs. To do this, the precipitated slurries are seeded with very fine magnetite powder. Adsorption and coagulation yield roughly magnetic flocculates which are then treated by magnetic separation. In a variant of this process, the metals are coprecipitated with a hydrated iron oxide that plays the role of a magnetic carrier.

Research was accordingly directed at the purification of an aqueous solution of cadmium sulfate concentrated to 1 mmol/1 (112 ppm Cd). After precipitation at pH 10.5, the supernatant contained less than 0.1 ppm Cd.

To conduct a separation, it is necessary to treat the solution by adding a certain proportion of iron salt, which, as it precipitates, imprisons the metal by adsorption/coagulation mechanisms.

2.1 Magnetic carrier

For magnetic purification to succeed, the hydrated iron oxide precipitated must have adequate magnetic properties for it to be retained in the extraction matrix. Tests were initially conducted with ferric nitrate and chloride (Figure 1). X-ray diffraction analysis showed that the products obtained in both cases had the structure of a goethite (ïFeOOH, of which the magnetic susceptibility measurement was relatively low. The floes formed contained a great deal of interstitial water, which considerably diluted their magnetic susceptibility. It was therefore necessary to find an iron salt whose precipitated hydroxide would have improved properties.

A mixture of ferric chloride and ferrous sulfate in the proportion of one mole of ferrous iron for two moles of ferric iron ('Fe3CV solution) yields excellent results (Figure 1). This proportion corresponds to that of a magnetite Fe/^. in fact, however, depending on the iron concentration of the solution, the product removed was identified by X-ray analysis as maghemite YFe_20_3. Maghemite is an unstable phase of hematiîe «$Fc?0_3$. with a spinel structure vhich. in drying, Splays *a.* spectrum ufTV?-' • "^

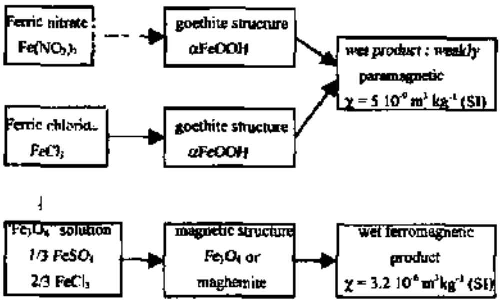

Figure 1 : Precipitates of different iron salts

Particle size measurements were taken on the precipitates produced by the 'Fe_30_4' solution alone (Figure 2). The curves were unimodal, relatively symmetrical, giving a fair idea of d50. The particle size measured was that of the floes as they occurred during their passage through the magnetic separator after a phase of intense stirring.

A precipitated '$Fej0_4$' solution containing 4.5 mol/1 of total iron reveals a d50 of nearly 15 ji.m, whereas a more concentrated solution at 7.5 mol/1 of total iron gives a d50 of 2.4 urn.

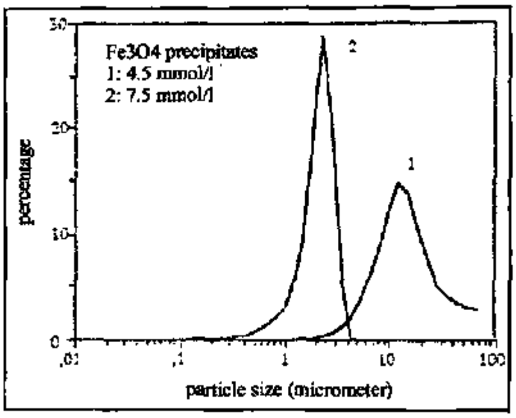

Figure 2: Particle size distribution of 'Fe-A,' precipitates

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2. '/ i 'ı_ r^ap $_{iet,c}$ separator and filtration ,i.-.et--s

VoKïï on magnetic sorting and purification cunduutîd at the LEM are performed on a superconducting magnetic separator. This is an extraction matrix separator, operating in cyclic mode, built by GEC/Alsthom (Figure 3).

A superconducting Nb/Ti coil is immersed in a cryostat filled with liquid helium (4.2 K). The canister containing the extraction matrix is positioned at the center of the cryostat. The matrix consists of fine ferromagnetic elements such as stainless steel foam or wool, beads, which, while maintaining high porosity, offer a large trapping surface area. The coil generates a high magnetic field (4000 kA/m) and a high field gradient which, by converging on the ferromagnetic matrix, generate a sufficient magnetic force to trap the very fine particles measuring a few pm and/or low magnetic particles.

The material is fed in the upper (or lower) portion of the system, regulated by pump. The slurry treated falls dirough the energized matrix. The magnetic particles remain trapped in the matrix, while the non-magnetic particles are recovered or recycled by a pump for a second purification. The magnetic field is then shut off, and the magnetic products trapped in the matrix removed by pressurized water jet and recovered (Figure 4).

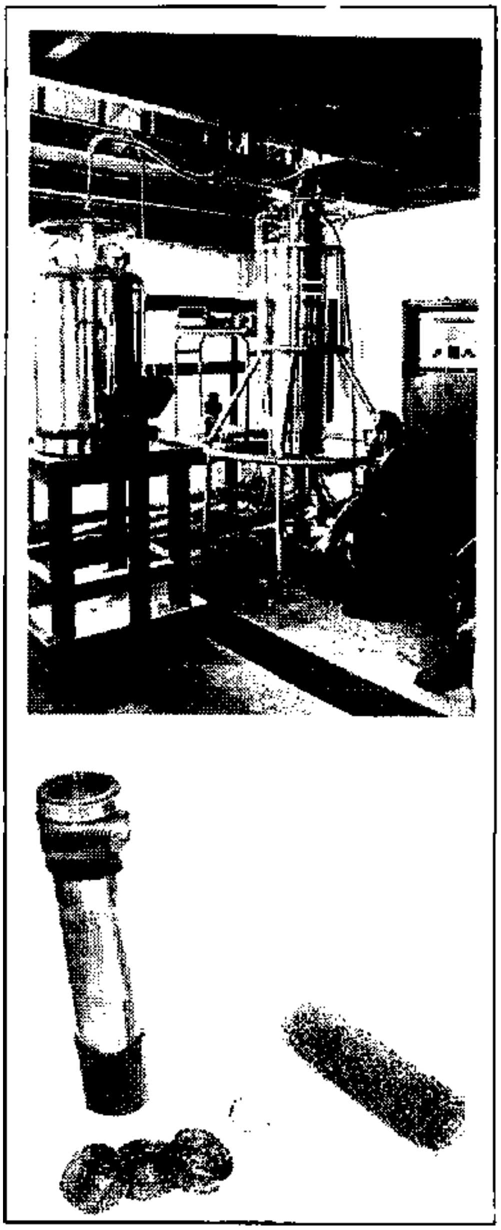

Figure 3: GEC/Alsthom superconducting separator matrices and canister

This system, if satisfactory for the purification of industrial minerals, is less effective for purifying fluids, because is results in the redilution of the pollution when the loaded magnetic 'floes' are expelled. For the treatment of polluted effluents, a washing system using a chemical solution allowing the breakup of the floes and the recovery of the metallic ions has been incorporated in the system. A rinsing technique with acid solution has been selected for cleaning the matrix. When the matrix loading limit is reached, the feed is turned off and the rinse solution is sent into the canister. It destroys the floes by solubilization and they are detached by losing their magnetic properties. The metallic ions go into the rinse solution, which can be used again until saturation. This operation, conducted under magnetic field, offers a threefold advantage:

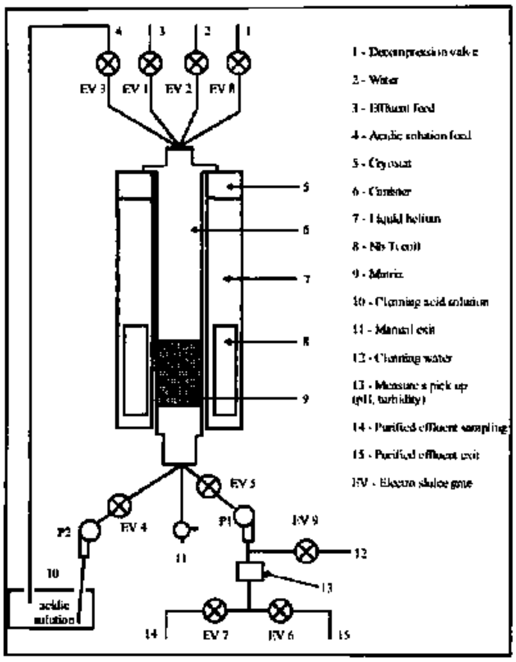

Figure 4: Fluid purification by magnetic separator

- smaller volumes of slurries (in the case of precipitation) hence greater ease of handling, storage or subsequent treatment,
- lower energy and operating costs of the system: the elimination of magnetic field cycles (operation in permanent field) helps to design coils featuring simpler technology and lower operating cost (lower helium consumption),
- the possibility of recovering metals by electrolysis or electrochemical methods (re-use of iron salts possible by recycling in precipitation).

2.2.2 Test results

The principle of strong-field/high-gradient magnetic separation consists of producing strong heterogeneities in an originally homogeneous outside magnetic field, using small ferro-magnetic elements. This results in force centres of small range, on which any paramagnetic substances will be trapped. The method is based on the use of magnetic-attraction forces, which retain paramagnetic particles in a solid/water suspension on magnetised matrix elements. Particles with a sufficiently high magnetic susceptibility and non-magnetic particles, i.e. the cleaned product, will flow out of the system. 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 particles. After this, the field is switched off and the magnetic particles are removed with a high-pressure water jet.

2.2.2.1 Separation tests on industrial minerals

Some magnetic separation tests have been conducted on this equipment in the area of purification of different minerals. The influence of some parameters has been studied (magnetic field intensity, material flow rate, matrix type, material size distribution).

a. Purification of nephelinic syenite

The comparative studies are tabulated in table 1. The results show that about 98 % of the iron and titanium contained in the original sample is held in the matrix and the non magnetic part is perfectly purified. With respect to previous studies on conventional separators (Low and High Intensity Magnetic Separation, LIMS and HIMS), the superconducting magnetic separation superiority is evident. The possibility of obtaining a magnetic field of 5 T is a favorable factor in achieving better results than those obtained by the traditional flow sheet (6 to 8 passes). An additional advantage of the new system is its possibility for the high rate recovery of fine particles (40 Jim) which are useless with the classical separators (the experimental study shows that a field of 2 or 3 T damages the quality of the final purified product).

b. Purification of glass sand

The purification of sand for glass industry by conventional methods consists of 4 to 6 passes in dry HIMS or 2 to 4 passes with wet HIMS and followed by flotation. In this case, only 1 pass is necessary in order to obtain a higher or equal degree of sand purification. For example, the purification of glass sand having 0,24 % Fe by the new separator (I pass at 5 T) gives a purified concentrate containing 0,025 % Fe while the product obtained from the same glass sand by the conventional flow sheet is about 0,06 % Fe (two passes at 1,8 T).

Table 1 - Comparison of results with conventional and superconducting separators on nephelinic syenite

Products	**Weight %**	Fe%	**TiO_2 %**	**Recovery** Fe%	**Recovery** TiO_2 %	Test **conditions**
Mag.	52,98	4,14	1,38	97,92	98,11	Panicle size : < 100 urn Magnetic field : 5 T Pulp : 20 % solid Feed velocity : 10 1/min Matrix : 300 mm of metallic tissue disks
Purified	47,02	0,09	0,030	2,08	1,89	
Feed	100,00	2,24	0,75	100,00	100,00	
Mag.	46,90	4,72	1,57	98,60	98,04	Particle size : < 50 urn Magnetic field : 5 T Pulp: 20%solid Matrix : Stainless steel wool: 300 mm
Purified	53,10	0,059	0,028	1,40	1,96	
Feed	100,00	2,25	0,75	100,00	100,00	
One pass on the superconducting solenoid separator						
Ferro Mag.	1,92	37,20	n.d	29,57	-	Particle size : < 280 urn 1 pass LIMS 5 passes of purified product Magnetic field : 1,8 T 4 gaps : 0,8 mm Pulp : 20 % solid Pulp velocity : 101/min
Mag.	66,74	2,44	n.d	67,43	-	
Purified	31,34	0,23	n.d	3,00	-	
Feed	100,00	2,41		100,00	100,00	
Mag.	8,96	0,46	n.d	1,81	-	Purified products reground to minus 100 urn 3 passes Conditions : the same
Purified	22,40	0,15	0,45	1,19	-	
Feed	31,34	0,238	-	3,00	100,00	
Nine passes on conventional LIMS and HIMS						

2.2.2.2 Purification of liquid effluents

A specific installation was designed for the processing of effluents through extraction of precipitated and co-precipitated metals as magnetic "floes", i.e. magnetic metal hydroxides and co-precipitated magnetic and/or non magnetic metal hydroxides. Removal of the floes from the matrix is obtained not by switching off the magnetic field, but by a simple chemical modification caused by rinsing of the matrix with an acid solution. This solution, after having stopped feed flow, is then charged with metals trapped in the matrix. The solution, whose volume is limited to that of the canister, can recirculate for a progressive charging with metals and until sufficient metals are contained for an electrolytic treatment. 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 needs no longer to be switched off, which makes coil technology simpler, and reduces the operating cost because less helium is used.

a. separation tests on synthetic materials

Several tests were made with synthetic materials. Table 2 shows, as an example, the results obtained on a product containing five metals in solution, i.e. 20 ppm of Cr, and 10 ppm each of Ni, Cu, Fe and Zn. The influence of the proportion of "Fe304" solution added to the solution containing the metals was then tested. To be safe, the pH of the solution was stabilised at 12 by adding NaOH. (Table 2).

Table 2: Purification of a polymetallic solution

mass ratio iron added /metals to be removed	%Fe (1)	%Cr 0)	%Ni (1)	% Zn (D	%Cu (1)
0	37.0	37.0	45.0	32.0	42.0
12	79.3	58.5	88.1	31.49	75.9
31	97.4	96.6	>99	86.3	>99
45	99.1	>99	>99	83.3	>99

(1) : %metal purified after magnetic treatment

By means of simple precipitation of the solution, without adding Fe, the purification percentage for each of the metals is only 40 % for one pass. Recycling the solution that was pre-purified in the separator does not improve this result. Everything that can be magnetically trapped was retained" during the first pass. It should be noted, however, that non-magnetic metals such as zinc or copper are retained in the same manner, thanks to coagulation and adsorption phenomena on the floes. 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 metal, it can be considered that all metal except zinc is retained in the separator during a single pass. The purification of zinc appears to be more complex. Because of the amphoteric character of zinc precipitates, both trapping by ferrous floes and/or co-precipitation are strongly reduced when the ratio Fe total / metals is low

b. separation tests on industrial effluents

Industrial fluids were also treated. They were mainly received from surface treatment facilities (rinse water). The predominant metal varied according to origin, between copper and zinc. Washing fluids from spent vanadium-based catalysts and solutions containing tin (glass manufacture) were also tested. The results are given in Table 3.

Table 3: Purification results for various industrial baths

majority metal (M)in effluent	concentration before magnetic treatment	concentration after cryomagnetic treatment	% purification
Cu	21.3	0.04	99.8
Zn	18.6	0.05	99.8
V	38.6	LD	100
Sn	6517.2	52	99.2

These different 'process' waters display a highly variable concentration of main dissolved metal, but, to a lesser degree, they also contain other dissolved metals which are often not quantified in the characteristics supplied by the industries, because considered secondary. Furthermore, these wash waters contain reagents (particularly foaming agents) necessary for upstream processes. For each fluid, preliminary tests must be conducted to determine the amounts of iron to the added to obtain an overall magnetic product, with the understanding that precipitable impurities other than dissolved metals also enter the trapping structures.

These effluents, precipitated at pH 9 to 9.5 in the presence of iron salt, are fed to the separator at maximum magnetic field (4000 kA/m) with throughputs from 10 to 12 l/min.

The matrix in the canister is a stack of grids 11 an in diameter and 35 cm high.

For each effluent treated, magnetic purification is optimal for a number of liters, after which purification quality deteriorates sharply. This degradation corresponds to the saturation of the matrix. The feed cycle must therefore be interrupted for an acid cleaning cycle.

If these results are scaled up to industrial scale operation with a retention matrix 0.5 m high with a surface area 1 m^2, for example, the throughputs would be about 100 m^3/h per m^1 of matrix surface area.

3 AUTOMATION OF THE SYSTEM

Precipitation/purification research for the depollution of industrial fluids containing dissolved metals have shown that a cryomagnetic separator helps to meet a number of environmental concerns arising in a number of production sectors.

The adaptation of the mineral sorting method to these effluent treatment problems demands a modification to the matrix rinsing system. For an industrial demonstration, this is only feasible if the system is fully automated.

The use of the separator in 'semi-automatic' mode led to the design of a flowchart for the fluids and/or slurry to be treated (Figures 5 and 6).

Based on the operating principle and the adjustments described above, the main automatic guidelines were accordingly identified. The use of *GraphCET* as a technique for describing the process sequences was selected, because of its great flexibility (Figure 7).

The main parameters used for developing the flow chart were the following:

- feed position: high.or low,
- type of feed: mineral or effluent,
- sampling and volume,
- feed rate, rinsing and matrix cleaning,
- number of cycles: feed, rinsing,
- continuous or cyclic operation,
- field increase/decrease control,
- magnetic and cryogenic field parameter monitoring.

The general structure of the *GraphCET* used here is more complicated than that of an industrial *GraphCET,* because all possible parameters are included, this structure comprises a common purification (or feed) unit for the treatment of minerals or effluents.

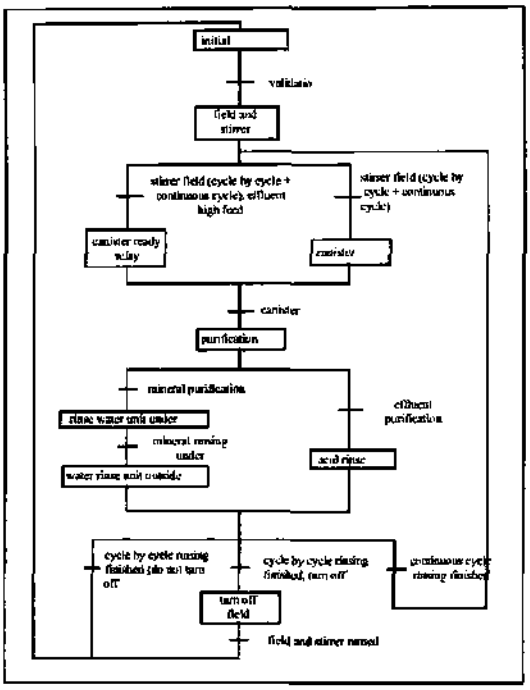

Figure 7: General *GraphCET*

This unit is divided into two branches depending on whether or not sampling is included. The *GraphCET* is then divided into two matrix rinsing units (water from bores, acid solution for effluents).

The water rinsing step for the purification of industrial minerals takes place in two stages (with and without field) to maintain the cycles of conventional separators. At the start of the operation, an initialization unit is used to input all the parameters (with choice of low or high feed), via the man/machine interface and the energization of the coil. The end of the *GraphCET* comprises the different branches necessary for cyclic operation (with or without field shutdown) and continuous operation. The *GraphCET* thus obtained is then programmed adequately for the PRC controller.

The controller has to be modulable, in order to evolve to account for additions of setpoints or equipment (preparation of feed, of solutions, pH monitoring, turbidity, throughput, matrix filling ratio). The controller selected here is a Toshiba EX100, which is modular and allows rapid upgradability of the system if necessary. Dialogue

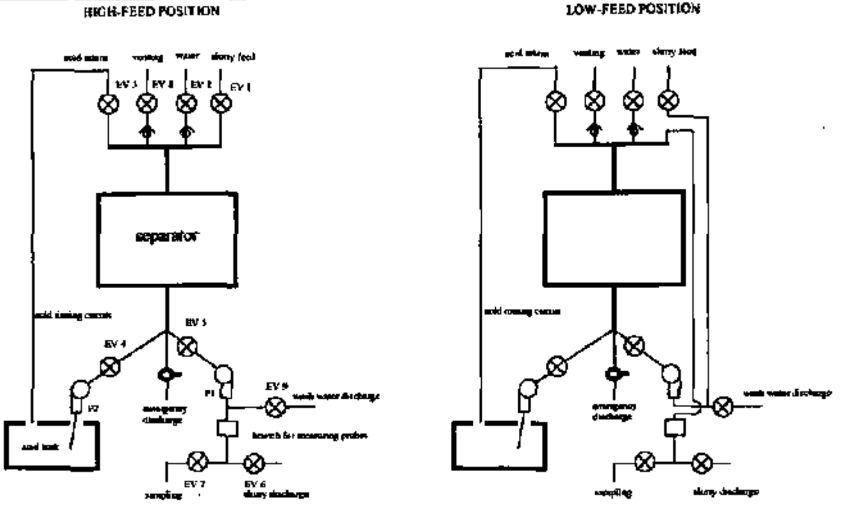

Figure 5: Block diagramme for industrial effluents

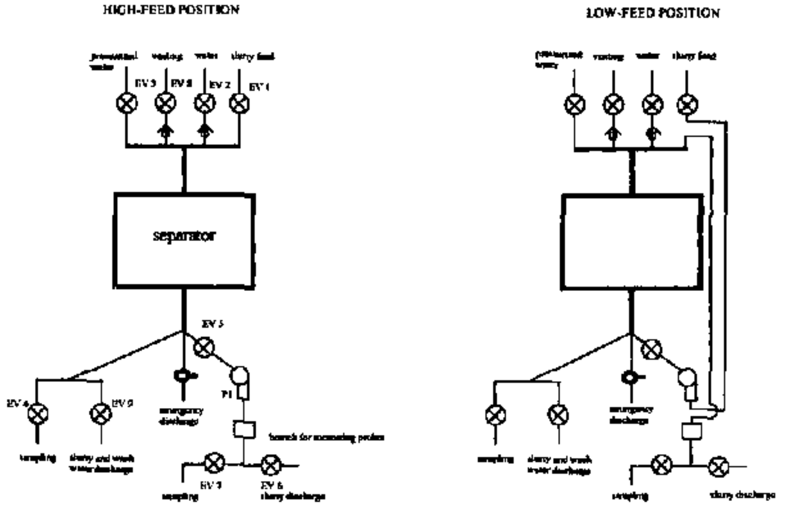

Figure 6: Mineral purification block diagram

for parameter input is achieved by a Quick Control LTD model QUO and both units are programmed by a PC compatible.

4 CONCLUSION

The process described in this article is used for the magnetic purification of large volumes of industrial fluids loaded with dissolved metals, without adding any solid phase or coagulent gel, as normally done in other water treatments applied today. The precipitated floes, trapped in a matrix, are recovered by acid dissolution in a volume that is twenty to fifty times smaller, depending on each case. This technique is mainly advantageous for very dilute effluents, which are difficult to treat by precipitation and settling or another costly method (reverse osmosis, microfiltration). In this process, the floes recovered in the acid display high metals reconcentration, allowing for subsequent treatment: reprecipitation for storage, or selective recycling of the metals for re-introduction into a manufacturing circuit.

Now that the possibility has been demonstrated of introducing reliable cryomagnetic systems offering simple operation into production systems (clay industry), the use of high magnetic fields should serve to:

- apply this method to effluents from chemical, hydrometallurgical, surface treatment industries,
- offer technically and economically advantageous solutions, which could supplant conventional processes in view of the operating criteria (higher throughputs, lower operating costs, reduced weight and size of the installations).

Since the system of cleaning by acid solution no longer requires turning off the magnetic field, the superconducting separator maintains the magnetic field without any electric power consumption, and die consumption of liquid helium is therefore considerably reduced.

The appearance of new superconducting materials at critical high temperature (ceramics) are likely to revolutionize the cryo-electricity market in the future, and allow rapid development of this technology and its applications, technico-economic studies have shown that the use of these new materials can achieve economies of around 20% in investment and operating costs.

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