



## Combined column and cell flotation process for the treatment of PAH contaminated hazardous wastes produced by an aluminium production plant

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### ABSTRACT

The aluminium electrolytic plants generate PAH and fluoride contaminated wastes which are usually classified as hazardous material. These residues are generally disposed in secure landfill sites. A flotation cell process was previously developed to remove PAH from these aluminium industry wastes. The tests were done on composite samples made of particle size fractions under 50 mm. The efficiency of the flotation cell process was demonstrated but the high quantity of concentrate produced (14.0%) during the air injection period, because of the solid entrainment, raised the treatment cost.

The aim of this study was to reduce the entrainment of fine particles in order to obtain an efficient and economic technology. The process initially developed was modified: the smallest particle size fraction (<0.5 mm) of the composite sample was treated in a flotation column, whereas the other particle size fractions (0.5–50 mm) were treated in a flotation cell. The separated treatment allowed to reduce the entrainment during the air injection period of the flotation cell step from 14.0% to 10.1%. The optimum total solids of the pulp and cocamidopropylhydroxysultaine (CAS) concentration were 3.33% and 0.50% (w w<sup>-1</sup>) for the flotation column, and 15% and 0.25% (w w<sup>-1</sup>) for the flotation cell. This combined flotation process minimized the total entrainment which allowed a 23.6% abatement of the concentrate quantity initially produced, and reduced the PAH concentrations of the wastes under the authorized limit of 1000 mg kg<sup>-1</sup>.

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### 1. Introduction

The aluminium electrolytic plant wastes are classified into three categories: atmospheric emissions, liquid effluents and solids. The atmospheric pollutants are particles, sulphur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), polycyclic aromatic hydrocarbons (PAH) and fluorinated compounds such as fluorinated hydrogen (HF), which are released during the anodes production, the electrolysis [1,2] and the aluminium casting. The liquid wastes concern process water, used for cooling during the metal casting and the anodes production, and draining water. These effluents are contaminated in organic matter, aluminium, fluoride, total suspended solids, oil, grease and PAH. The solids residues are red mud with high-metal oxides [3], PAH contaminated black sludge [4], spent pot linings with high-leachable toxic elements, alumina-contaminated foams, domestic and hazardous wastes [5]. The majority of the aluminium plant wastes are treated before recycling or burring. For example, the gas emissions are treated with gas purifier, the liquid wastes are sent to a wastewater plant, the spent pot linings [6] and the foams are

decontaminated and recycled. The hazardous wastes are disposed in secure landfills in the United States. The management of the hazardous wastes remains an issue and has to be reevaluated due to the scarcity of secure landfills.

A Söderberg aluminium smelter produces several hazardous wastes with different sizes during the anodes production, the electrolysis step and the aluminium casting. These residues are equipments of primary aluminium production (crucibles, electrolytic cells residues, horizontal and vertical Söderberg studs, anodic pastes, sheets), starting materials (carbon, alumina, pitch), finished products (aluminium) and cleaning wastes (ventilator and scavenger cleaning residues). PAH are ones of the pollutants encountered in such residues due to the Söderberg technology [7,8] which is characterized by the baking anodes inside the electrolytic cell. The amount of PAH measured can be strongly reduced with the prebake technology.

PAH are the results of incomplete organic matter combustion [9]. They may contain two or more fused aromatic rings without heteroatoms [10]. The USEPA has classified 16 PAH as probable human mutagens and carcinogens [11–13]. The regulatory limit for these compounds is fixed at 1000 mg kg<sup>-1</sup> except for the fluoranthene witch is at 10,000 mg kg<sup>-1</sup> in the province of Quebec (Canada). The limit for the benzo(b)fluoranthene, the benzo(j)fluoranthene and the benzo(k)fluoranthene, is either 1000 mg kg<sup>-1</sup> for each if they

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### Nomenclature

BJK	benzo(b+j+k)fluoranthene
BTA	waste before treatment
CAS	cocamidopropylhydroxysultaine
C1A	concentrate of the flotation column
C1B	concentrate of the flotation cell
CMC	critical micelle concentration
Ec	new composite sample
Ec <sub>i</sub>	initial composite sample
PAH	polycyclic aromatic hydrocarbons
PCB	polychloride biphenyl
R1A	refuse of the flotation column
R1B	refuse of the flotation cell
TS	total solids
USEPA	United States Environmental Protection Agency

can be analysed separately or 1000 mg kg<sup>-1</sup> for the sum of these compounds.

In the aluminium industry, PAH are produced during the transformation of alumina in aluminium in the electrolytic horizontal or vertical Söderberg stud cells [14]. More precisely, PAH are the results of anodes burnings made of coal tar pitch and coke.

In order to characterize and study the hazardous aluminium wastes, Bongo et al. [5] crushed and screened each kind of wastes sampled in six particle size fractions: <0.5, 0.5–1, 1–2, 2–8, 8–50, and >50 mm. PAH are concentrated in the particle size fractions lower than 50 mm. The highest concentrations were measured in the ventilator (2100 mg kg<sup>-1</sup> for BJK in the 0.5–1 mm size fraction) and scavenger (2500 mg kg<sup>-1</sup> for BJK in the 2–8 mm size fraction) cleaning residues [5]. The >50 mm size fraction was not contaminated by PAH so Bongo et al. [15] worked on a composite sample made of the five lowest size fractions to develop a treatment process in order to eliminate the PAH. This composite, named Ec, had a total PAH concentration of 2848 ± 1059 mg kg<sup>-1</sup>, a chrysene concentration of 565 ± 200 mg kg<sup>-1</sup> and a BJK concentration of 1130 ± 405 mg kg<sup>-1</sup> [5].

The treatments of the PAH contaminated soil are based on degradation or removal methods. The degradation can be biological [16–18], physical [19,20], chemical [21–24] or physicochemical methods [25]. The removal is done by leaching or flotation with surfactant [4,5,15,26–29].

Surfactants have both a hydrophilic head and a hydrophobic tail [30,31]. They are classified as anionic, cationic, non-ionic and amphoteric. CAS is an amphoteric surfactant as it has a positive charge on the quaternary amine group and a negative charge on the SO<sub>3</sub><sup>-</sup> group. Surfactants can assemble in the bulk solution into aggregates known as micelles [29,32]. The concentration at which the surfactants begin to form micelles is named critical micelle concentration (CMC) [33].

The flotation is a hydrometallurgical technique used for the treatment of inorganic (metals) or hydrophobic organic contaminated (PAH, PCB and hydrocarbons) soils and sediments [4,34,35]. It is based on the natural or activated surface properties of the particles and consists on air injection in order to transport out of the system the hydrophobic and unwanted particles [36].

A flotation process using 0.25% (w w<sup>-1</sup>) of CAS was operated on a composite sample made of several hazardous residues by Bongo et al. [5]. This treatment allowed a yield of 66% of BJK removal, which was sufficient to reach the regulatory limit of 1000 mg kg<sup>-1</sup>. However, the implementation of this technology method is unflavored by the high quantity of concentrate produced (14%) which should be managed as a hazardous waste. In order to reduce the cost of

the technology and increase its acceptability, the entrainment of fine particles has to be minimized. This phenomenon allowed the smallest particles to reach the concentrate during the air injection step of the flotation. The flotation columns are known to reduce the entrainment due to their geometry and their hydrodynamic characteristics [37].

The purpose of this study was to determine the feasibility and the efficiency of a separated treatment for fine particles in flotation column while the coarse particles are treated in flotation cell. The particle size fractions, the conditioning, the TS of the pulp and the surfactant concentration were the parameters experimented for the tests in the flotation column. The efficiency of the treatment was based on the PAH removal and the entrainment rates. The parameters were selected in order to maximize the collision between the particles and the air bubbles, to avoid the sedimentation, to obtain a high quality of the foam and to minimize the solids entrainment.

## 2. Materials and methods

### 2.1. Aluminium hazardous wastes

The aluminium hazardous wastes were sampled in a Söderberg aluminium production plant located in Québec (Canada). They were randomly selected with a shovel on a 1 m<sup>2</sup> surface inside different tubs outside the plant. The wastes collected were crucibles and electrolytic cells residues, ventilator and scavenger cleaning residues and floor sweepings. All the wastes were preserved at room temperature (22 ± 2 °C) and lightproof 20 L polypropylene containers.

Aluminium hazardous wastes were first characterized according to the procedure described by Bongo et al. [5]. The crushing and screening had done six particle size fractions: <0.5, 0.5–1, 1–2, 2–8, 8–50, and >50 mm.

### 2.2. Surfactant

The surfactant used in this study was the cocamidopropylhydroxysultaine, usually named CAS. It's a zwitterionic surfactant which properties are shown in Table 1. The surfactant CAS (Chemron, USA) was used as received.

### 2.3. Flotation column

The flotation column used measures 135 cm high with a 5 cm inside diameter. The column bottom was conical and contained an air sparger. A stirrer with five blades connected to a Caframo

**Table 1**  
Cocamidopropylhydroxysultaine (CAS) properties.

Physical and chemical properties	
Formula	
MW (g mol <sup>-1</sup> )	436
pH	6.5–8.0
Density	1.106
Solids (% w w <sup>-1</sup> )	49.0–51.0
Free amine (% w w <sup>-1</sup> )	1.0 (max)
Amine HCl (% w w <sup>-1</sup> )	1.0 (max)
Sodium chloride (% w w <sup>-1</sup> )	6.5 (max)

**Table 2**  
Flotation parameters.

Parameters flotation	Parameters controlled	
	Cell	Column
Flotation apparatus geometry	–	–
Waste particle size fraction	×	×
Pulp total solids	×	×
Mixing period		
Agitation	○	○
Time	○	○
Conditioning period		
Agitation	○	○
Time	○	○
Surfactant		
Nature	×	–
Concentration	×	×
Flotation period		
Number	×	–
Air flow	–	–
Agitation	○	×
Time	×	–

(–) Not tested; (×) directly tested; (○) indirectly tested.

motor was used to maintain agitation. The column was feed with a Cole-Parmer peristaltic pump. The concentrate was recovered by overflow at the top and the refuse was bleed with a peristaltic pump at the bottom. A washing water system was installed above the column.

#### 2.4. Flotation cell

Flotation was also performed in a Wemco mechanically agitated cell with a 2 L spitzkasten tank. A mixer and a diffuser mechanism allowed the air introduction and provide a 3000 rpm mixing action on the pulp.

#### 2.5. Column and cell flotation parameters selection

A flotation process is controlled by different parameters (Table 2). In this study, some of them were voluntarily neglected (flotation apparatus geometry, air flow rate), others were selected on the Bongo et al. [5,15] experiences results (surfactant nature) and some were directly (surfactant concentration, pulp TS, particle size fraction) or indirectly tested (stirring intensity, residence time) (Table 3). The geometry of the flotation apparatus was not evaluated because only one kind of cell and column were available. The air flow rate during the flotation period could not be controlled in the cell due to the air mode injection by subaeration. The air flow rate in the column was calculated according to the air surface flow recommended [37] fixed between 0.015 and 0.02 m s<sup>-1</sup>. The stirring intensity and the residence time in the cell flotation were reduced and adjusted on the foam quality basis visually evaluated. The selection parameters order is illustrated by Fig. 1.

#### 2.6. Effect of the particle size fraction on the flotation column process

The effect of the particle size fraction of the waste on the flotation process was studied using 50 g of <0.25 and <0.5 mm particle size fractions, which were mixed with 2 L of tap water in Pyrex beakers during 10 min and under a 800 rpm agitation speed. After this period, 0.25% (w w<sup>-1</sup>) (50 mg) of CAS was added to the pulp and a conditioning period of 20 min (800 rpm) was observed. The pulp was then transferred in the flotation column with a peristaltic pump. The stirring was maintained for 10 min under an 800 rpm agitation speed. The conditioning period in the column allowed the degassing of the pulp and, consequently, minimized the entrainment. A flotation period of 10 min with a 1.94 L min<sup>-1</sup> air flow rate was operated. The foam produced during the flotation period was recovered in a pan, filtered under vacuum with a Whatman

**Table 3**  
Parameters and values tests for the flotation.

Parameters	Bongo et al. [15]	Bongo et al. [15]	Bongo et al. [5]	Current	Current
Hazardous waste					
Nature	Composite	Composite	Composite	Composite	Composite
Particle size	<8 mm	<8 mm	<50 mm	<250/<500 μm	500 μm to 50 mm
Apparatus	2 L beaker	Wemco cell flotation	Denver cell flotation	Column flotation	Wemco cell flotation
Pulp					
TS (% p p <sup>-1</sup> )	10	7/10/15/20	15	1.25/1.67/3.33/6.67	15
Mixing					
Time (min)	–	–	10	10	10
Agitation (rpm)	–	–	1800	800	1500
Conditioning					
Surfactant					
Nature	Tw80/TrX100/CAS/BW	CAS	CAS	CAS	CAS
Conc. (% p p <sup>-1</sup> )	0.5	0/0.1/0.2/0.25/0.5	0.25	0.25/0.50/0.75/1.0	0.10/0.25/0.50/1.0
Time (min)	60	60	2 × 30	30	30
Agitation (rpm)	–	1800	1800	800	1500
Flotation					
Number	–	3	2	1	1
Air flow (L min <sup>-1</sup> )	–	1	1	1.94	1
Time (min)	–	7, 5, 2	7, 5	10	10
Agitation (rpm)	–	1800	1800	800	1500
BJK removal (%)	35	57–68	47–83		
Entrainment (%)	–	10	9–18		

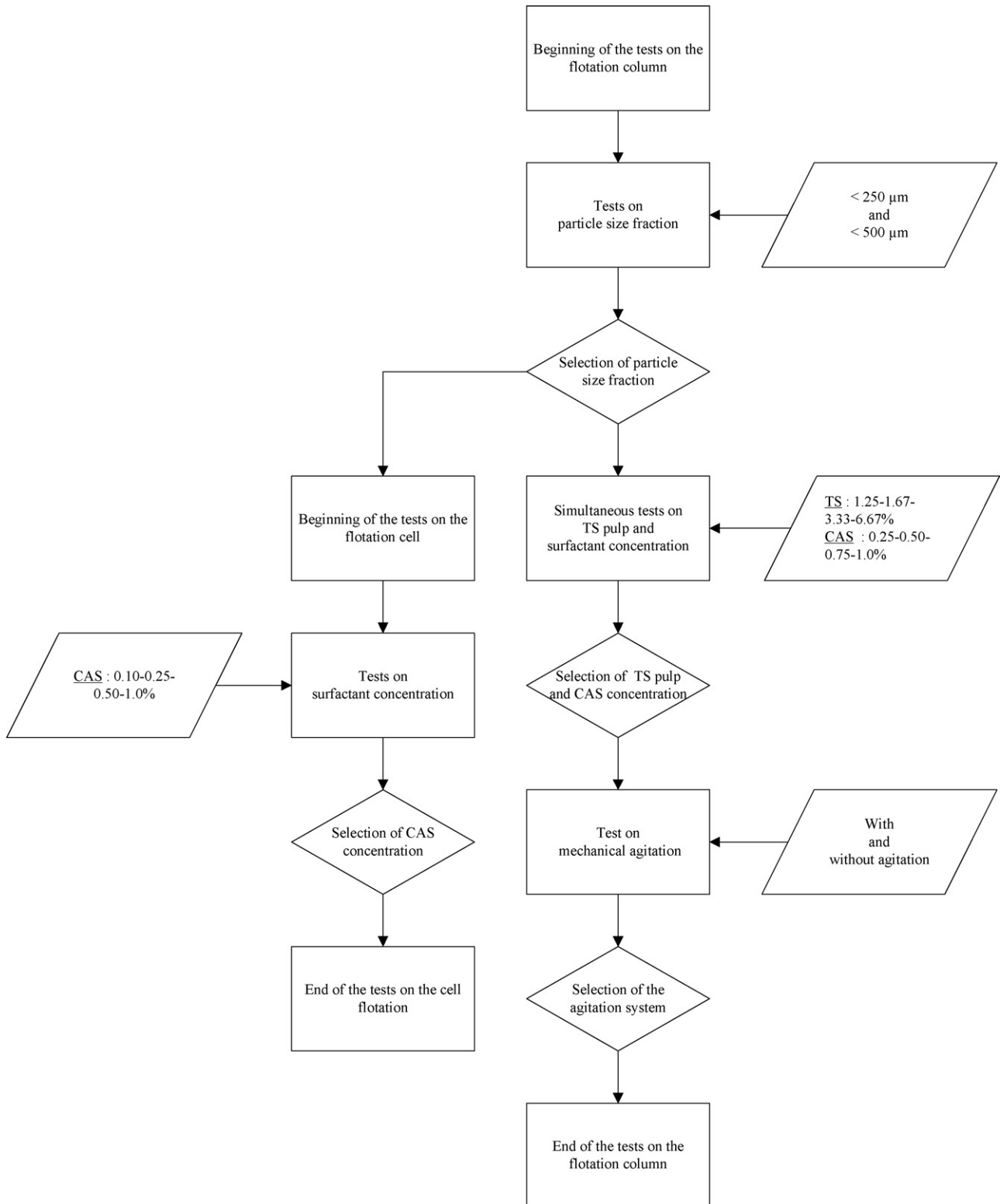


Fig. 1. Experiments summary.

qualitative No. 4 (pore size = 20–25 μm) paper filter and dried during 24 h at 60 °C in an oven. This foam was the concentrate of the flotation and named C1A. The remaining pulp in the column, designed as the refuse and named R1A, was extracted at the bottom with a peristaltic pump, filtered under vacuum with a Whatman No. 4 paper filter and dried during 24 h at 60 °C.

### 2.7. Effect of TS and CAS concentration on the flotation column process

The study of the effect of TS concentration was carried out using 25, 50 and 100 g of a <0.5 mm particle size fraction, which were mixed with tap water (1.5 or 2.0L) in a 4L Denver tank with a

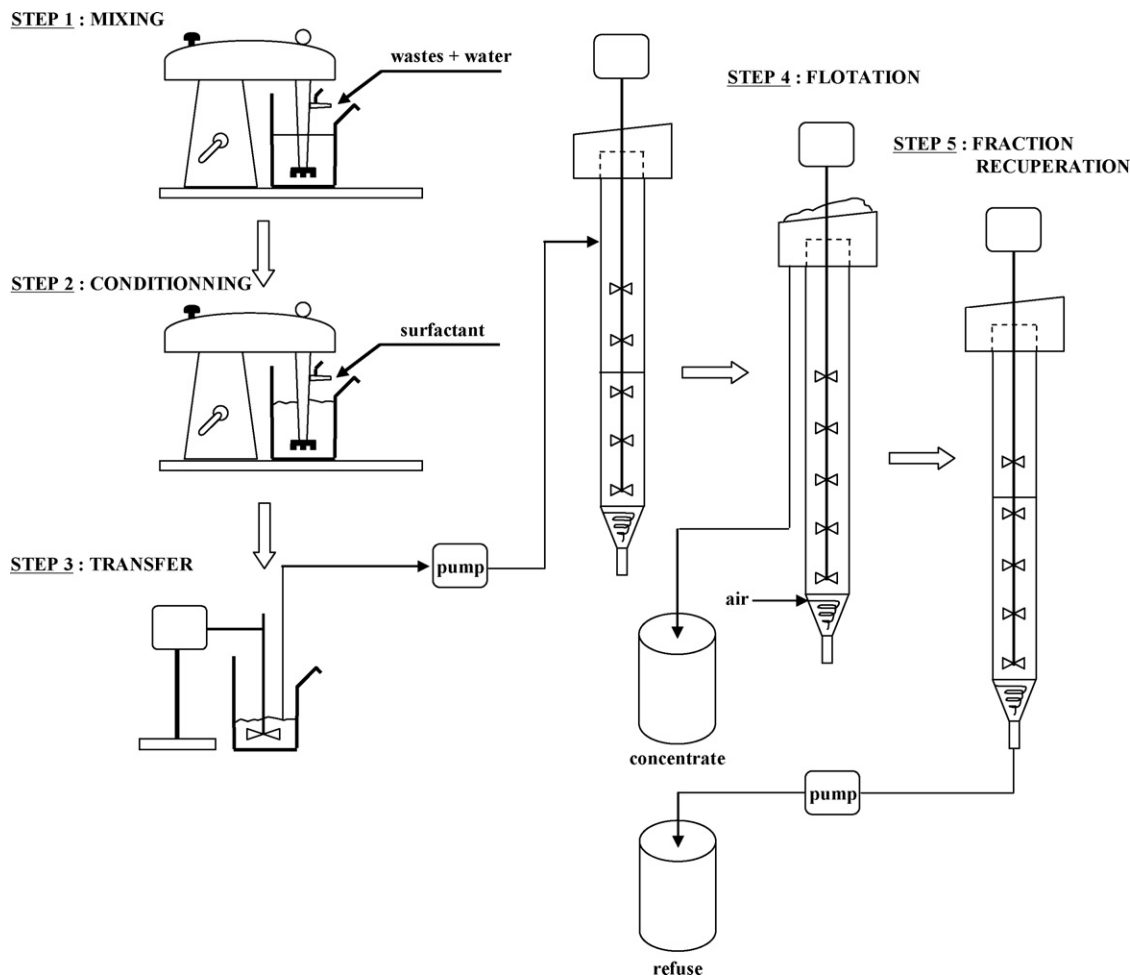


Fig. 2. Column flotation experimental setup.

Wemco flotation cell during 10 min and under a 1500 rpm agitation speed. After this period, 0.25, 0.50, 0.75 or 1.0% ( $w w^{-1}$ ) of CAS was added to the pulp and a conditioning (1500 rpm) period of 20 min was observed. The pulp was then transferred in the flotation column with a peristaltic pump. The stirring was maintained at 800 rpm for 10 min after the transfer. A flotation period of 5 min with a  $1.94 L min^{-1}$  air flow rate was applied (Fig. 2). In the cases of the experiments carried out at TS = 1.25% and 1.67%, the time of the flotation period was reduced from 10 to 5 min due to the absence of foam after 5 min. In contrary, a second flotation period was necessary for the experimentations with the pulp at 3.33% and 6.67% ( $w w^{-1}$ ) TS. In these cases, the pulp volume was higher than the column capacity, because of the foam formation, so the transfer was done in two times. The foam produced during the flotation period was recovered in a pan, filtered under vacuum with a Whatman No. 4 paper filter and dried during 24 h at 60 °C. This foam was the concentrate of the flotation and named C1A. The remaining pulp in the column, designed as the refuse and named R1A, was extracted at the bottom with a peristaltic pump, filtered under vacuum with a Whatman No. 4 paper filter and dried during 24 h at 60 °C.

### 2.8. Effect of CAS concentration on the flotation cell process

A mass of 150 g of the new composite sample (Ec) and 1 L of water were mixed in a 2 L Wemco tank with a Wemco cell for 10 min

under a 1500 rpm agitation speed. Then, 0.10%, 0.25%, 0.50% or 1.0% ( $w w^{-1}$ ) of CAS was added to the pulp. This one was conditioned (1500 rpm) during 30 min before the flotation period of 10 min. The foam produced was collected in a Pyrex pan and dried during 24 h at 60 °C (Fig. 3). This fraction was named C1B. The pulp remaining in the tank was decanted with ferric chloride (0.2 mL of a commercial ferric chloride solution (11% Fe,  $w w^{-1}$ ) per litre of refuse) and Percol 765 (10 mL of a polymer solution ( $1 g L^{-1}$ ) per litre of refuse). The solids named R1B were dried in an oven during 24 h at 60 °C.

### 2.9. Analytical

#### 2.9.1. PAH Soxhlet extraction

PAH were extracted from solid phase according to the USEPA method No. 3540C [38] and the MENVIQ MA 400-PAH 1.1 method. Between 1.0 and 2.0 g of dry sample were weighed in a cellulose extraction thimble. A volume of 250  $\mu L$  of a surrogate recovery standard was added to the surface sample in the thimble with a 500  $\mu L$  syringe. The surrogate recovery standard used was a 1000  $mg L^{-1}$  solution of  $d_{10}$ -anthracene (Aldrich). Then, the thimble was placed in a Soxhlet extractor attached to a 30 mL round bottom flask containing dichloromethane. The sample was extracted for 16–24 h at 100 °C. The extract was cooled after the extraction was completed. The extract volume was adjusted to 25 mL with dichloromethane. If the extract volume was higher than 25 mL, the volume was reduced with air. The extract was preserved in amber bottle at 4 °C.

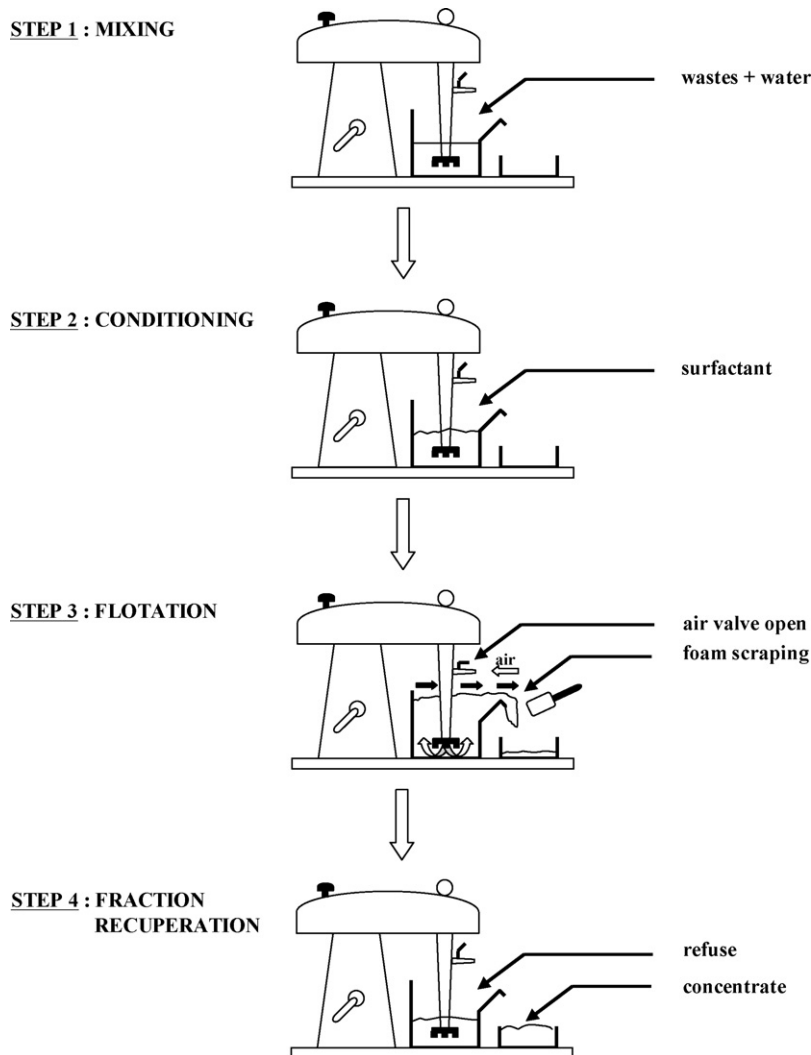


Fig. 3. Cell flotation experimental setup.

### 2.9.2. PAH analysis

PAH in samples were measured with a gas chromatograph coupled with a mass spectrometer (apparatus PerkinElmer, model Clarus 500). 16 PAH were checked.  $d_{10}$ -Anthracene used as surrogate recovery standard allowed the determination of the extraction

efficiency.  $d_{10}$ -Phenanthrene was used as internal standard. Calibration standards were prepared through dilution of a Mix commercial solution (8270/625/CLP/appendixIX Semivolatile Calibration Mix,  $1000 \text{ mg L}^{-1}$ ). This solution contained naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluor-

**Table 4**

PAH concentration ( $\text{mg kg}^{-1}$ ) of the particle size fractions of hazardous wastes.

PAH	Size fraction (mm)			
	<0.25	<0.50	0.50–50 (Ec)	<50 <sup>a</sup> (E <sub>c</sub> )
Fluoranthene	158 ± 17	151 ± 10	125 ± 11	130 ± 70
Pyrene	206 ± 25	194 ± 16	136 ± 13	155 ± 80
Benzo(a)anthracene	247 ± 52	254 ± 26	137 ± 28	195 ± 110
Chrysene	711 ± 126	898 ± 122	508 ± 67	565 ± 200
Benzo(b,j,k)fluoranthene	1349 ± 82	1589 ± 139	802 ± 251	1130 ± 405
Benzo(a)pyrene	239 ± 89	179 ± 19	69 ± 21	105 ± 60
Indeno(1,2,3-cd)pyrene	454 ± 173	324 ± 57	124 ± 42	230 ± 130
Dibenzo(ah)anthracene	128 ± 49	128 ± 14	69 ± 33	115 ± 95
Benzo(g,h,i)perylene	420 ± 94	378 ± 63	156 ± 40	255 ± 140
∑ PAH	3828 ± 582	4095 ± 332	2126 ± 452	2848 ± 1059
CV (%) <sup>b</sup>	15	8	21	37
n <sup>c</sup>	6	16	7	71

<sup>a</sup> values obtained by Bongo et al. [15] for the initial composite sample.

<sup>b</sup> CV = coefficient of variation.

<sup>c</sup> n = number of sample analysed.

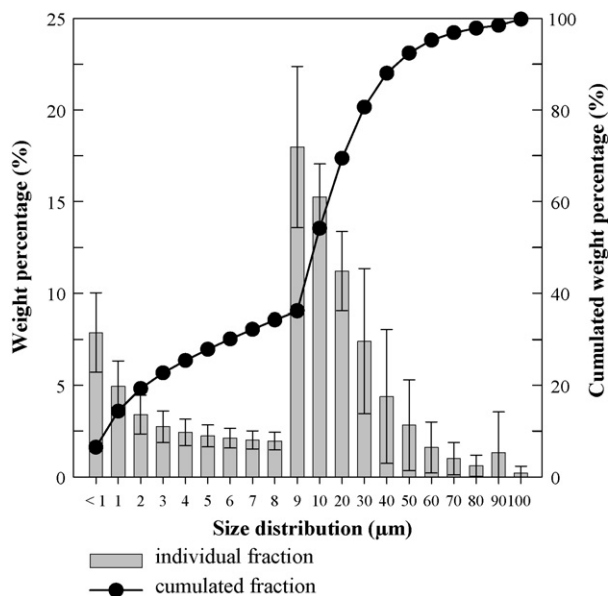


Fig. 4. Particle size distribution of the concentrates produced during the air injection period of the flotation cell process applied on the initial composite  $Ec_i$ .

anthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3,c-d)pyrene, dibenzo(ah)anthracene and benzo(g,h,i)perylene.  $d_{10}$ -Anthracene and benzo(j)fluoranthene were added to the Mix solution through individual commercial solution at  $1000 \text{ mg L}^{-1}$ .  $d_{10}$ -Phenanthrene was added to each sample. The internal standard concentration was  $2.5 \text{ mg L}^{-1}$  in each sample analysed. Five standards were prepared for the calibration (0, 0.5, 1, 2.5 and  $5 \text{ mg L}^{-1}$ ). The apparatus used did not allowed the distinction between benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k)fluoranthene because their retention time were too close to each other. So, one signal corresponds to these three PAH, which was called BJK in this study.

### 3. Results and discussion

#### 3.1. Composite characterisation

The initial composite sample  $Ec_i$  characterised by Bongo et al. [5] was modified because the smallest particle size fraction of the hazardous wastes was treated separately in this study. The mass percents of the particle size fractions were adjusted in order to keep the TS of the pulp at 15% in the flotation cell [15]. The new composite  $Ec$  was made of the following particle size fractions: 12.2% of 0.5–1 mm or 0.25–1 mm, 14.5% of 1–2 mm, 18.8% of 2–5 mm and 54.5% of 5–50 mm.

The new scheme of treatment had an impact on the matrix contents. Indeed, the composite  $Ec$  treated in the flotation cell presented a lower total PAH concentration ( $2126 \pm 452 \text{ mg kg}^{-1}$ ) (Table 4) than the initial composite  $Ec_i$  ( $2848 \pm 1059 \text{ mg kg}^{-1}$ ). The BJK concentration in the 0.5–50 mm fraction was now below the norm ( $802 \pm 251 \text{ mg kg}^{-1}$ ). The smallest particle size fractions (<0.25 and <0.5 mm) processed in the flotation column had a higher total PAH concentration ( $3828 \pm 582$  and  $4095 \pm 332 \text{ mg kg}^{-1}$ ) than the composites  $Ec_i$  and  $Ec$ . The BJK was not the only PAH above the regulatory limit. The chrysene was the second most concentrated PAH found in the wastes, but the measured concentrations were below the norm ( $<1000 \text{ mg kg}^{-1}$ ) for all particle size fractions. The PAH contamination was strongly associated with the fines particles. The modification of the initial PAH concentrations of the composite may affect the efficiency of the treatment such as the surfactant concentration or the TS concentration of the pulp.

#### 3.2. Flotation column process

##### 3.2.1. Effect of the particle size distribution

A granulometric laser assay (Fritsch 22 analysette, 016–1160  $\mu\text{m}$ ) was done on three concentrates produced during the air injection period of the flotation cell with 0.25% ( $w w^{-1}$ ) of CAS on the initial composite  $Ec_i$  [15]. The results showed that the concentrates were made of particles smaller than 0.2 mm (Fig. 4). Consequently, to minimize the entrainment during the flotation cell process, the particles smaller than 0.2 mm had to be removed from the initial composite  $Ec_i$  and treated separately.

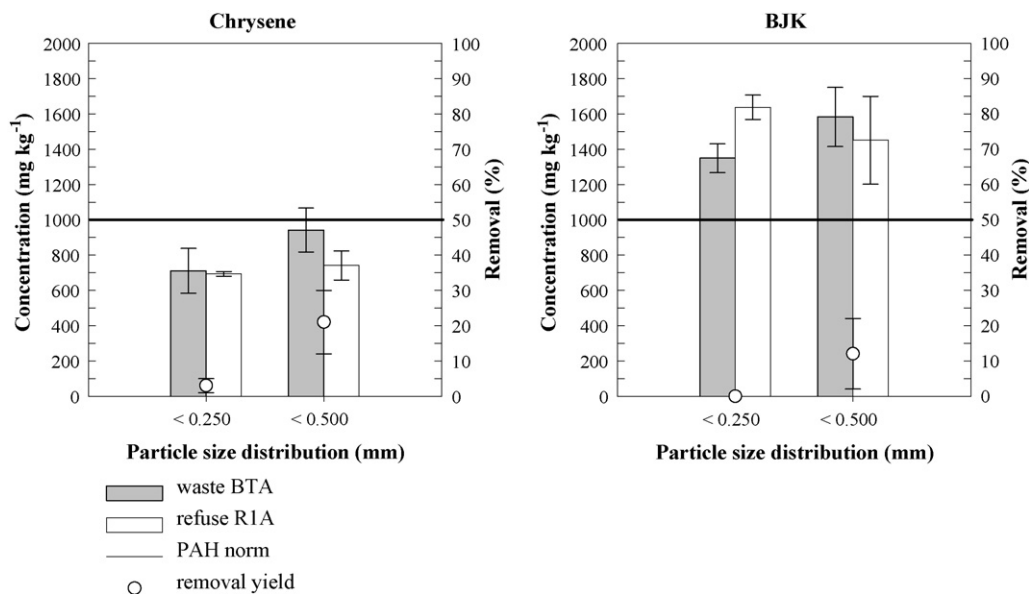


Fig. 5. PAH concentration and removal yield of the <0.5 and <0.25 mm particle size fractions before (BT) and after (RIA) the treatment in flotation column (TS = 2.5%,  $w w^{-1}$ ) with CAS (0.25%,  $w w^{-1}$ ).

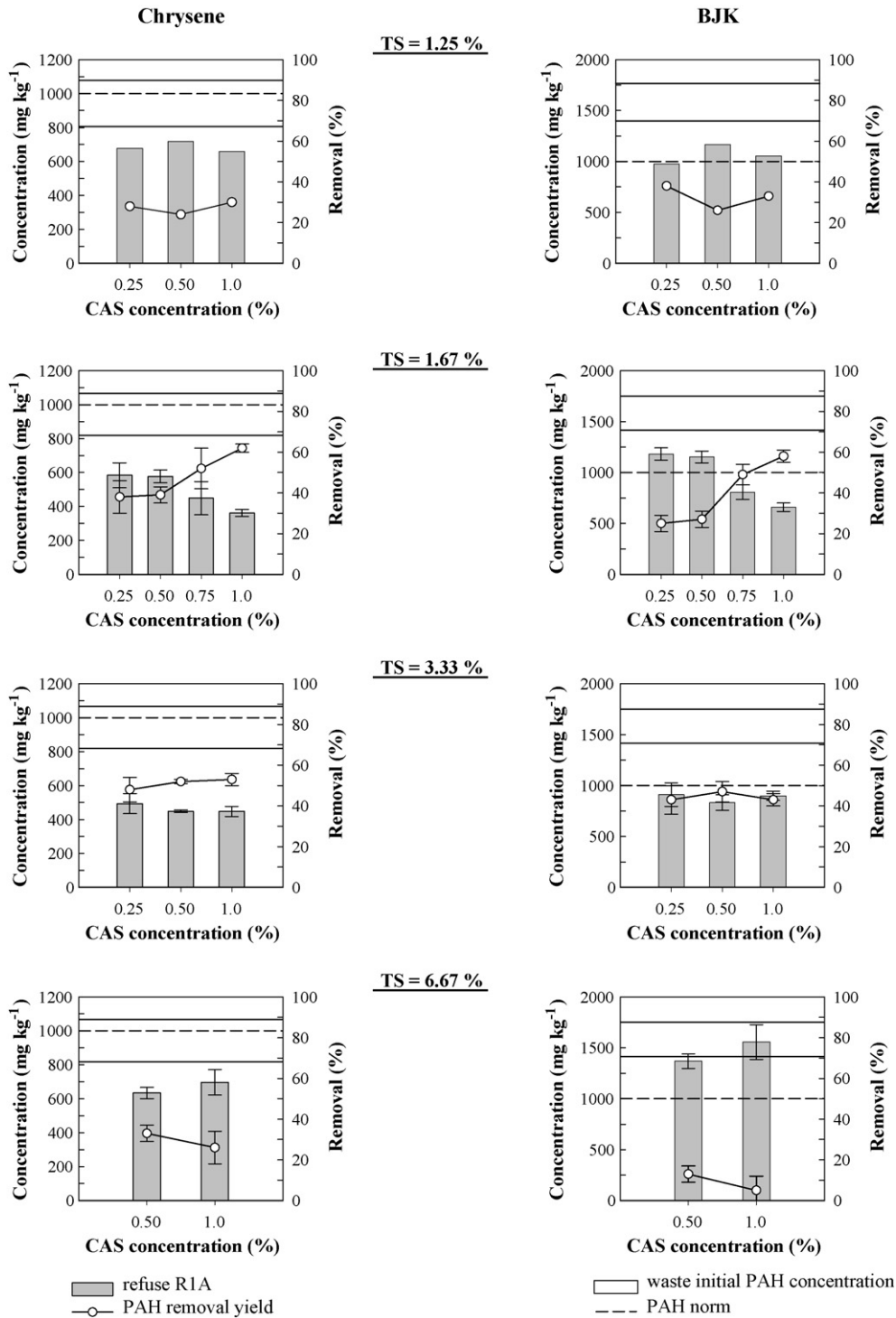


Fig. 6. PAH concentration and removal yield of (R1A) after the treatment in flotation column on the <0.5 mm particle size fraction with different TS and CAS concentrations.

The flotation column treatment was then operated on two particle size fractions (<0.25 and <0.5 mm), in order to determine the particle diameter impact on the collision and attachment efficiencies, which allow the aggregate formation in the bulk area. A difference was observed for the PAH removal yields between the two particle size fractions tested (Fig. 5). The flotation column on the <0.5 mm particle size fraction allowed to reach removal yields of 21% and 12% for the chrysene and BJK, respectively, whereas for the <0.25 mm particle size fraction, the removal yields were under 5%.

These results were not correlated to the material balance. Indeed, the refuse recoveries (84.6% and 85.1%) and the entrainment rates (5.53% and 5.20%) were the same in the two cases.

The process efficiency with the <0.5 mm particle size fraction may depend on the highest collision and attachment probabilities between the particles and the air bubbles and on the longest residence time of the particles in the bulk due to their weight. The cut point for the separated flotation treatment of the smallest particles must be 0.5 mm. The PAH removal yields obtained did not allowed



to reach the limited value of  $1000 \text{ mg BJK kg}^{-1}$ . The conditioning method, the TS of the pulp, the surfactant concentration and the aeration rate may have an effect on the process efficiency. These parameters may be optimized in order to check the feasibility of the treatment of the smallest particle size fraction in a flotation column. The mixing and conditioning of the pulp were modified in order to obtain good froth (foam) production. These parameters were adjusted for the tests on the TS of the pulp and the CAS concentration.

### 3.2.2. Effect of the TS and CAS concentration

A flotation column process on a pulp at 1.25% of TS and with CAS concentration at 0.25%, 0.50% or 1.0% ( $\text{w w}^{-1}$ ) allowed to reach chrysene concentration under the  $1000 \text{ mg kg}^{-1}$  limited value (Fig. 6). The removal rates were between 24% and 30%. For the BJK, the concentrations remained next to the norm. The same process on a pulp at 1.67% of TS gave best results with CAS concentration above 0.75% ( $\text{w w}^{-1}$ ) (above 52% of removal for the chrysene, and 49% for the BJK). The chrysene and BJK removal rates increased with the CAS concentration in this case. With a pulp at 3.33% of TS, the flotation efficiency was improved with CAS concentration at 0.50% or 1.0% ( $\text{w w}^{-1}$ ) (removal of 52% and 53% for the chrysene, 47% and 43% for the BJK). The flotation process lost efficiency with a pulp at 6.67% of TS. The refuse PAH concentrations increased with the concentration in this case.

The PAH concentrations of the refuse reached values under the norm when the flotation was done on a pulp at 1.67% of TS and with

0.75% or 1.0% ( $\text{w w}^{-1}$ ) of CAS. A good efficiency was also obtained with TS of the pulp at 3.33% and a CAS concentration at 0.50% ( $\text{w w}^{-1}$ ). The selection of the flotation parameters depends on the removal rates obtained and on the entrainment (Fig. 7). The concentrate quantity produced during the flotation was higher (14.1% and 20.1%) with a pulp at 1.67% of TS with 0.75% or 1.0% ( $\text{w w}^{-1}$ ) of CAS than a pulp at 3.33% of TS with 0.50% ( $\text{w w}^{-1}$ ) of CAS (12.5%). The best parameters for the flotation were a pulp at 3.33% of TS and a CAS concentration at 0.50% ( $\text{w w}^{-1}$ ).

A pulp at 1.25% of TS did not contained enough particles so the collision probability between particles and air bubbles was too low for PAH removal. The CAS concentration increase affected the entrainment and not the removal rates. A pulp at 1.67% of TS seemed to increase the collision probabilities between particles and air bubbles because the removal rates were higher in comparison with a pulp at 1.25% of TS. However, the CAS concentration increase was responsible of a higher entrainment. A pulp at 3.33% TS allowed the reduction of the entrainment as it seems that with this pulp density the equilibrium between electrostatic and gravitational forces favours sedimentation of the mineral part and attachment of PAH to air bubbles. A pulp at 6.67% of TS was above the optimal value because a great fall in efficiency was observed. The numerous particles in the pulp provoke sedimentation.

After the flotation column process, the PAH were distributed between the concentrate and the refuse (Fig. 8) depending on the TS of the pulp and the CAS concentration. The PAH remained mainly in the refuse when the flotation process was applied on a pulp

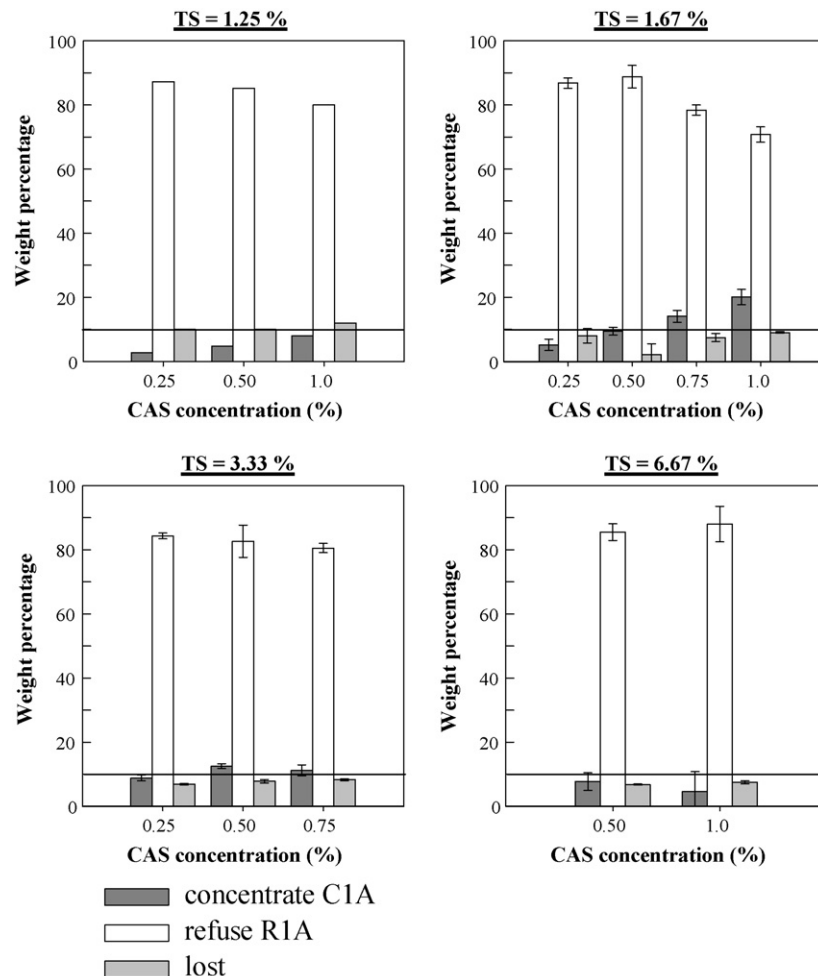


Fig. 7. Mass balance after the treatment in flotation column on the  $<0.5 \text{ mm}$  particle size fraction with different TS and CAS concentrations.

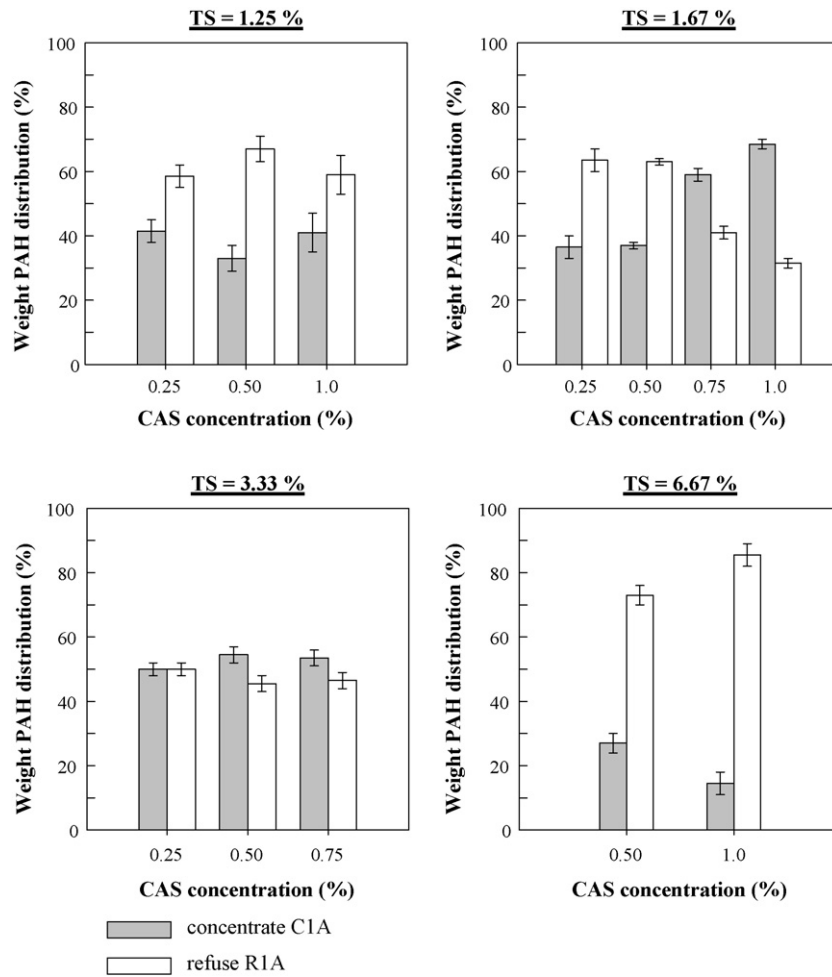


Fig. 8. PAH distribution (weight) after the treatment in flotation column on the <0.5 mm particle size fraction with different TS and CAS concentrations.

at 1.25% of TS. The same observation was done with the pulp at 1.67% of TS and the CAS concentration at 0.25% and 0.50% ( $w w^{-1}$ ). The tendency turned over with the CAS concentration augmentation (0.75 and 1.0%,  $w w^{-1}$ ). The distribution was balanced with the pulp at 3.33% of TS. The PAH remained in the refuse with a pulp at 6.67% of TS. The highest PAH quantity observed was in the concentrate produced during the flotation of a pulp at 1.67% of TS and with a CAS concentration of 0.75% or 1.0% ( $w w^{-1}$ ). These results were positively correlated with the entrainment which was responsible of the presence of a part of the PAH in the concentrate.

### 3.2.3. Impact of the mechanical agitation

The flotation columns are not mechanically agitated at industrial scale. The mixing was omitted in order to check if the potential of the process was dependent or not on the agitation system. The tests were run with the parameters previously selected. The chrysene and BJK removal rates reached each 43% and the entrainment was at 12.4%. These results confirmed that the mechanical agitation was not necessary in the column. The aeration was sufficient to maintain the pulp mixing. The absence of the mechanical agitation allows decreasing the operation cost of the process.

### 3.3. Flotation cell process

The efficiency of the flotation cell process was tested in order to check the effect of the <0.5 mm particle size fraction suppression.

Four CAS concentrations were experimented: 0.10%, 0.25%, 0.50% and 1.0% ( $w w^{-1}$ ). The best concentration (0.25%,  $w w^{-1}$ ) was the same as determined in the study of Bongo et al. [5]. The removal yields for chrysene and BJK were 72% and 71%, respectively (Fig. 9), compare to 69% and 66% for the same treatment on the composite Ec<sub>i</sub>. In this configuration, the entrainment reached 10.1% (Fig. 10). The separated treatment in column of the <0.5 mm particle size fraction allowed to reduce the entrainment and to improve the PAH removal during the air injection period of the flotation cell on the new composite Ec. The results obtained may depend on the lowest initial PAH concentrations of the composite Ec and on the highest collision efficiency due to the highest particles diameter.

The PAH distribution between the concentrate and the refuse depended on the CAS concentration (Fig. 11). The PAH recovery in the concentrate decreased with the CAS concentration due to the foam quality and the entrainment. The quantity of PAH in the concentrate was optimum (75%) with a CAS concentration of 0.25% ( $w w^{-1}$ ).

### 3.4. Flotation scheme

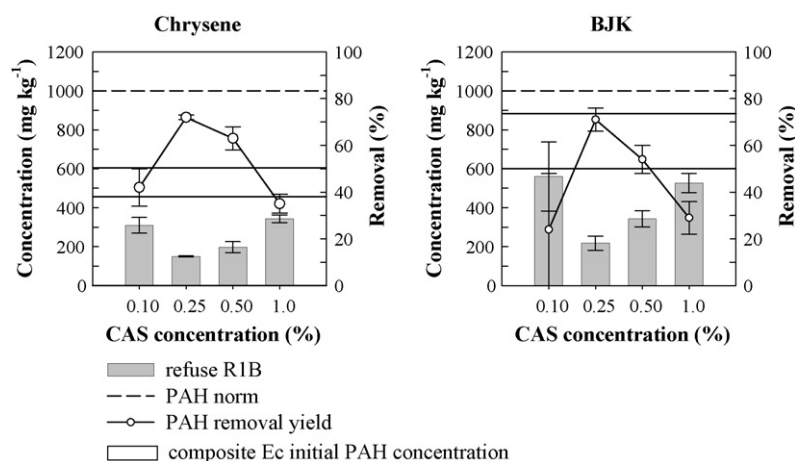
The separated treatment of the smallest particle size fraction (<0.5 mm) in a flotation column was significant but the modifications brought to the initial process affect the treatment line arrangement, its operation and its cost (Table 5). However, the new process appears more advantageous even if an additional screen

**Table 5**  
Advantages and disadvantages of the initial and improved processes.

Parameters	Bongo process		Improved process		Advantage	Disadvantage
	1		1	2		
<b>Wastes preparation</b>						
Crushing	–		–	–		
Screening	50 mm		50 mm	500 $\mu$ m		□
<b>Wastes treatment</b>						
Apparatus	Cell		Cell	Column		□
<b>Pulp</b>						
Wastes quantity (g)	150		150	50	200	□
Process water (L)	1		1	1.5	2.5	□
TS (%)	15		15	3.33	–	
<b>Surfactant</b>						
Concentration (%)	0.25		0.25	0.50	0.31	□
<b>Mixing</b>						
Time	–		10	10	–	□
Agitation	–		1500	1500	–	□
<b>Conditioning</b>						
Time	60		30	20+10	–	□
Agitation	1800		1500	1500+800	–	□
<b>Flotation</b>						
Number	2		1	1	–	□
Air flow rate ( $L \text{ min}^{-1}$ )	1		1	1.94	–	
Time	7 and 5		10	10	–	□
Agitation	1800		1500	–	–	□
<b>Efficiency</b>						
BJK removal (%)	66		71	43	53	
Entrainment (%)	14.0		10.1	12.4	10.7	□

and a flotation column are required. Indeed, several flotation cells were initially included in the treatment line so one of them could be substituted by a flotation column. Furthermore, this configuration allows a higher wastes treatment quantity per batch. The improvement of the flotation step was especially observed by the reduction of the concentrate quantities produced. The combination of the column and the cell generated 107 kg of concentrate per tonne of hazardous wastes treated, which represented a decrease of 23.6% compared to the 140 kg per tonne produced by the process developed by Bongo et al. [5]. The PAH removal yields were not improved (46% versus 69% for the chrysene and 53% versus 66% for the BJK), but the PAH concentrations in the refuse remained under the limited value of 1000 mg kg<sup>-1</sup> (260 mg kg<sup>-1</sup> versus 175 mg kg<sup>-1</sup> for the

chrysene and 465 mg kg<sup>-1</sup> versus 384 mg kg<sup>-1</sup> for the BJK). The new process included an increase of 25.0% of the surfactant consumption (3.12 kg per tonne of hazardous wastes treated versus 2.5 kg t<sup>-1</sup>) and 87.7% of the water consumption (12.5 m<sup>3</sup> per tonne of hazardous wastes treated versus 6.66 m<sup>3</sup> t<sup>-1</sup>). Nevertheless, the CAS cost remains lower than the disposal cost of the concentrate and the water process can be reused and recirculated so the flotation step is more economical in this case. The time treatment reduction from 60 to 40 min and the mechanical agitation speed decrease from 1800 to 1500 rpm are also beneficial points. A preliminary cost analysis confirmed the new process potential (Table 6). Indeed, the operational cost is reduced with the column flotation introduction and allows a 12\$ saving per ton of wastes treated which



**Fig. 9.** PAH concentration and removal yield (RIB) after the treatment in flotation cell (TS = 15%, w w<sup>-1</sup>) on the >0.5 mm particle size fraction (Ec) with different CAS concentrations.

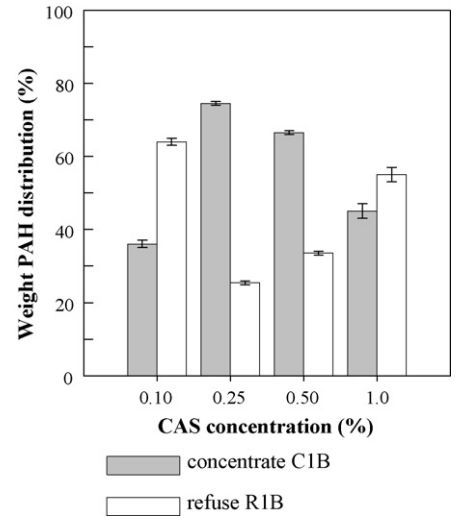
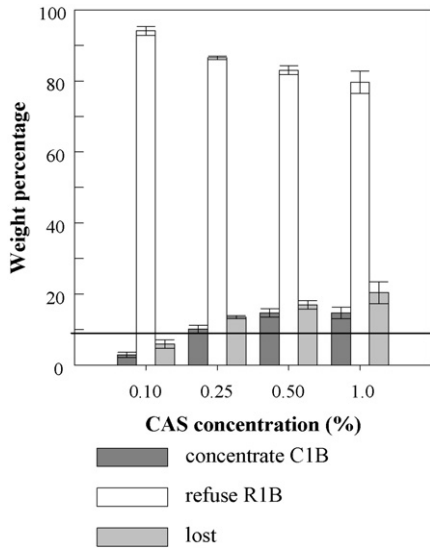


Fig. 10. Mass balance after the treatment in flotation cell (TS = 15%,  $w w^{-1}$ ) on the >0.5 mm particle size fraction (Ec) with different CAS concentrations

Fig. 11. PAH distribution (weight) after the treatment in flotation cell (TS = 15%,  $w w^{-1}$ ) on the >0.5 mm particle size fraction (Ec) with different CAS concentrations.

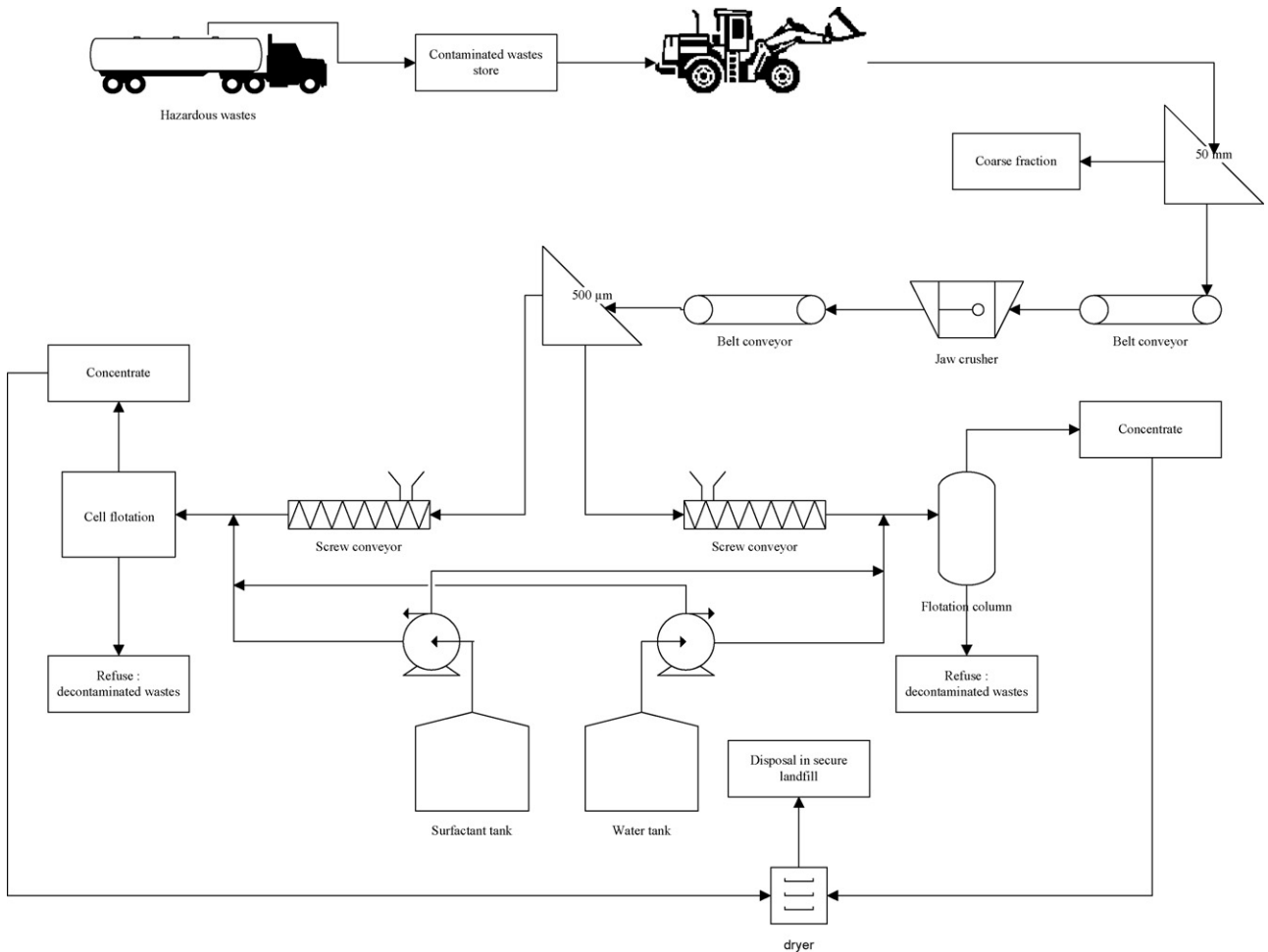


Fig. 12. Industrial process scheme.

**Table 6**

Preliminary cost analysis of the treatment process for 4000 t of wastes treated per year.

	Initial process	Improved process
Infrastructure	\$379,613	\$379,613
Transportation equipment	\$400,000	\$400,000
Wastes preparation equipment	\$113,000	\$152,000
PAH treatment equipment	\$678,500	\$681,500
Total equipment	\$1,571,113	\$1,613,113
Equipment installation	\$1,099,779	\$1,129,179
Total equipment and installation	\$2,670,892	\$2,742,292
Debt servicing <sup>a</sup>	\$668,942	\$686,825
Total plant cost	\$3,344,710	\$3,434,124
Plant cost per treated ton	\$42 t <sup>-1</sup>	\$43 t <sup>-1</sup>
Direct operating costs	\$123 t <sup>-1</sup>	\$114 t <sup>-1</sup>
Total plant and operating costs	\$165 t <sup>-1</sup>	\$157 t <sup>-1</sup>

<sup>a</sup> Payment period: 5 years; annual interest rate: 8%; amortization period: 20 years.

largely offset the moderate plant cost augmentation. Consequently, the scheme of the process developed by Bongo et al. [5] can be changed. The new process includes a parallel flotation treatment of the <0.5 mm fraction in a column flotation and a treatment of the >0.5 mm fraction in a cell flotation. The concentrates produced are sent to disposal as hazardous waste and the refuses are mixed together in order to carry out the next step of the whole process (Fig. 12).

#### 4. Conclusion

The flotation process initially developed by Bongo et al. [15] was improved. The treatment of the <0.5 mm particle size fraction of the hazardous wastes in a flotation column and the treatment of the >0.5 mm particle size fractions in a flotation cell allowed to remove PAH (72% for chrysene and 71% for BJK) and to reduce the total entrainment during the flotation step (from 14.0% to 10.7%). The impact was significant on the concentrate quantities sent to treat as hazardous waste (a 23.6% decrease). The parameters selected for the column and flotation cell scheme were a TS pulp of 3.33% and a CAS concentration of 0.50% (w w<sup>-1</sup>) for the column and a TS pulp of 15% and a CAS concentration of 0.25% (w w<sup>-1</sup>) for the cell. These values allowed to obtain a good PAH removal and a low entrainment.

The flotation was the first step of the whole process developed for the decontamination of the PAH and fluoride contaminated hazardous wastes. The second step will consist on the fluoride removal and/or stabilization. This has already been tested but the impact of the modification applied at the flotation scheme has to be evaluated. The next stage of the research will be the experimentation of the whole process including the recirculation of the effluents produced.

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