Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 2925136 C 2023/08/01

(11)(21) 2 925 136

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 2016/03/24
(41) Mise à la disp. pub./Open to Public Insp.: 2017/09/24
(45) Date de délivrance/Issue Date: 2023/08/01

(51) Cl.Int./Int.Cl. *B01D 21/26* (2006.01), *B01D 21/01* (2006.01)

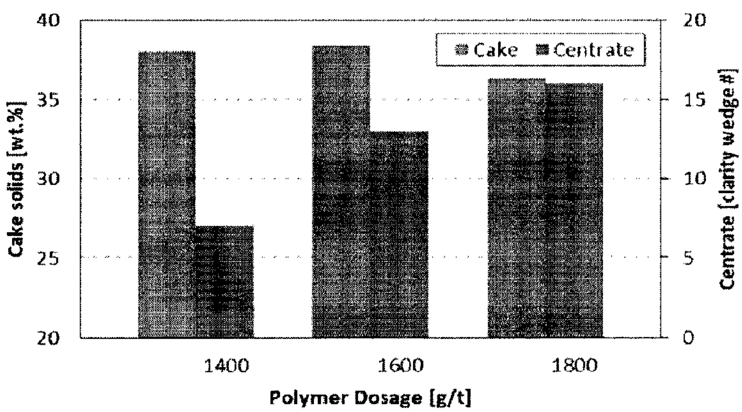
(72) Inventeurs/Inventors:
DANG-VU, TRONG, CA;
RAMEY, SCOTT, US;
KLEIN, COLIN, CA;
DICKSON, KEN, CA;
NELSON, AJITH, CA

(73) Propriétaire/Owner:
SNF GROUP, FR

(74) Agent: WILSON LUE LLP

(54) Titre : METHODE DE TRAITEMENT DES MATIERES EN SUSPENSION DE PARTICULES MINERALES DANS L'EAU PAR CENTRIFUGATION AU MOYEN D'UN TRAITEMENT POLYMERE SYNTHETIQUE DOUBLE

(54) Title: METHOD FOR TREATING SUSPENSIONS OF MINERAL PARTICLES IN WATER BY CENTRIFUGATION USING A DUAL SYNTHETIC POLYMER TREATMENT



Solids content of centrifuge cake vs. anionic polymer (AF) dosage

(57) Abrégé/Abstract:
Method for treating an aqueous suspension of mineral particles comprising sequentially:
- adding an anionic flocculant in the suspension,
- mixing the resulting treated suspension,
- adding a cationic flocculant having a molecular weight mote than 2 millions daltons or a cationic coagulant having a molecular weight less than 1 million daltons in the suspension,
- mixing the resulting treated suspension,
- centrifuging the resulting mixture.

ABSTRACT

Method for treating an aqueous suspension of mineral particles comprising sequentially:

- adding an anionic flocculant in the suspension,
- mixing the resulting treated suspension,
- adding a cationic flocculant having a molecular weight mote than 2 millions daltons or a cationic coagulant having a molecular weight less than 1 million daltons in the suspension,
- mixing the resulting treated suspension,
- centrifuging the resulting mixture.

METHOD FOR TREATING SUSPENSIONS OF MINERAL PARTICLES IN WATER BY CENTRIFUGATION USING A DUAL SYNTHETIC POLYMER TREATMENT

FIELD OF THE INVENTION

The invention relates to a method for treating a suspension of mineral particles in water by centrifugation using a dual synthetic polymer treatment in a specific sequence before the centrifugation step.

Suspensions of mineral particles in water include all types of tailings, or waste materials. The suspensions result from mineral ores processes. They are for instance industrial tailings and all mine wash and waste products resulting from exploiting mines, such as, coal mines, diamonds mines, phosphate mines, metal mines (alumina, platinum, iron, gold, copper, silver, etc...). Suspensions can also result from drilling mud or tailings derived from the extraction of bitumen from oil sand. These suspensions generally comprise mineral particles such as clays, sediments, sand, metal oxides, and may contain oil mixed with water.

In particular, the invention relates to the treatment of oil sand tailings by centrifugation.

BACKGROUND OF THE INVENTION

The treatment of tailings has become a technical, environmental and public policy issue.

It is common practice to use synthetic or natural polymers such as coagulants and flocculants to separate the solids from the liquid.

For a long time, and even nowadays, mineral tailings produced by physical or chemical ore treatment methods have been stored above ground in retention lagoons, ponds, dam or embankments in semi-liquid form. These large volumes of stored tailings therefore create a real hazard, notably if the dikes break.

The improvement of chemical and mechanical treatments of tailings is therefore a great challenge that needs to be addressed.

Various attempts were made in the past decades to improve the treatment of tailings in order to efficiently recycle water and reduce the volume of tailings ponds. Basically two types of method have been developed to treat tailing and separate solids from water: physical treatment and chemical treatment.

The main physical treatments include centrifugation, filtration, electrophoresis and electro-coagulation.

On the other hand, chemical methods are emerging. They include process involving the addition of chemicals such as sodium silicate, organic flocculants, inorganic coagulants, oxidizing and reducing agents and carbon dioxide.

Centrifugation technology has been used for many years in the treatment of tailings. The principle of centrifugation is to use centrifugal force to separate water out of tailings. By spinning the mixture in a large cylindrical vessel at high speeds, typically between 1,000 and 3000 rotations per minute (rpm), the water is forced from the tailings mixture. This results in a cake of solids that may be discharged in a dedicated area, as well as recovered water.

Flocculants have been used to improve the centrifugation performances. Gypsum and flocculant have also been used in oil sands tailings treatment; however, the effectiveness is limited due to difficulties in the preparation of gypsum slurries and the negative effect of calcium concentration in water recycled back to the process.

Oil sands are a mixture of bitumen, sand, fine clays and small amounts of water. Bitumen is typically separated from the oil sands ore by a hot water extraction process. This results in the formation of large volumes of tailings waste. Coarse sand tailings settle quickly and are used to form dykes and beaches, however fine clay tailings settle slowly and over 3 to 5 years settle to a solids content of approximately 30 wt.% after which additional settling becomes slight. These fine tailings are referred to as mature fine tailings (MFT). Accumulation of tailings, especially MFT, is a significant issue for the Oil Sands Industry and as a result numerous technologies have been implemented to dewater these tailings.

The document “Dry Stackable Tailings as a Tailings Management Option: Preliminary Laboratory and Field Experience Using Centrifuges” (Mikula,et al., Proceedings of the Canadian International Petroleum Conference 2009, Canada 2009) discloses the use of flocculants to improve the dewatering of mature fine tailings by centrifugation.

Despite great advances in research over the last 10 years, there is still a need to develop new solutions to decrease centrifuge cake volume by increasing cake solids content, and to increase the quality of recovered water by reducing its solids content. There is a great need to recycle the recovered water in order to use it immediately back to the process.

SUMMARY OF THE INVENTION

The present invention addresses the above needs by providing a method for improving the treatment of suspensions of solid particles in water thanks to the use of a dual synthetic water soluble polymer treatment in a specific sequence before the centrifugation.

According to the invention, it was found that the addition into the tailings of an anionic flocculant, followed by the addition of a cationic flocculant or a cationic coagulant before the centrifugation may significantly improve the performances of centrifugation. It may decreases centrifuge cake volume and increases the quality of recovered water at a such level that said recovered water can be used immediately back to the process. This may considerably reduce operation cost.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a method for treating an aqueous suspension of mineral particles comprising, sequentially:

- adding an anionic flocculant in the suspension,
- mixing the resulting treated suspension,
- adding a cationic flocculant or a cationic coagulant in the suspension,
- mixing the resulting treated suspension,
- centrifuging the resulting mixture.

The flocculant and/or coagulant are added either into a pipe transporting the suspension, or either into a vessel containing the suspension.

Anionic flocculant

In the present invention anionic flocculant is preferably a synthetic water soluble polymer and is obtained advantageously by the polymerization of at least one non-ionic monomer and at least one anionic monomer.

The anionic flocculant has an anionicity preferably ranging from between 10 to 70 mol%, preferably from 20 to 40 mol %. The molecular weight of the anionic flocculant is preferably comprised between 5 and 40 million daltons, and more preferably between 10 and 20 million.

Cationic Flocculant

In the present invention cationic flocculant is preferably a synthetic water soluble polymer and is advantageously obtained by the polymerization of at least one non-ionic monomer and at least one cationic monomer. The molecular weight of the cationic flocculant is more than 2 millions daltons.

The cationic flocculant has a cationicity preferably ranging from between 20 to 100 mol%, preferably from 40 to 80 mol %. The molecular weight of the cationic flocculant is preferably comprised between 5 and 40 millions daltons, and more preferably between 7 and 20 millions.

Cationic coagulant

In the present invention cationic coagulant is preferably a synthetic water soluble polymer and is obtained advantageously by the polymerization of at least one non-ionic monomer and at least one cationic monomer. The molecular weight of the cationic coagulant is less than 1 million daltons.

The cationic coagulant has a 100% cationicity and molecular weight of the cationic coagulant is preferably comprised between 50.000 and 1 million daltons, and more preferably between 200.000 and 1 million.

Monomers

The monomers useful for the preparation of the water soluble polymer according to the invention, are described hereafter.

Non-ionic monomers are preferably selected from the group comprising acrylamide; methacrylamide; N-mono derivatives of acrylamide; N-mono derivatives of methacrylamide; N,N derivatives of acrylamide; N,N derivatives of methacrylamide; acrylic esters; and methacrylic esters.

The most preferred non-ionic monomer is acrylamide.

Anionic monomers are preferably selected from the group comprising monomers having a carboxylic function and salts thereof; monomers having a sulfonic acid function and salts thereof; monomers having a phosphonic acid function and salts thereof. They include for instance acrylic acid, acrylamide tertio butyl sulfonic acid, methacrylic acid, maleic acid, itaconic acid; and hemi esters thereof.

The most preferred anionic monomers are acrylic acid, acrylamide tertio butyl sulfonic acid (ATBS), and salts thereof. Generally, salts are alkaline salts, alkaline earth salts or ammonium salts.

Cationic monomers are preferably selected from the group comprising dimethylaminoethyl acrylate (DMAEA) quaternized or salified; dimethylaminoethyl methacrylate (DMAEMA) quaternized or salified; diallyldimethyl ammonium chloride (DADMAC); acrylamidopropyltrimethylammonium chloride (APTAC); methacrylamidopropyltrimethylammonium chloride (MAPTAC).

Monomers having a hydrophobic character may also be used as a comonomers for the preparation of the water soluble polymer (anionic or cationic) but at a concentration in weight based on the total monomer content of less than 5%. They are preferably selected from the group comprising (meth)acrylic acid esters having an alkyl, arylalkyl or ethoxylated chain; derivatives of (meth)acrylamide having an alkyl, arylalkyl or dialkyl chain; cationic allyl derivatives; anionic or cationic hydrophobic (meth)acryloyl derivatives; and anionic or cationic monomers derivatives of (meth)acrylamide bearing a hydrophobic chain.

Polymers of the invention are linear or structured. As is known, a structured polymer is a polymer that can have the form of a star, a comb, or has pending groups of pending chains on the side of the main chain. The polymers of the invention, when structured, remain water soluble.

The polymerization can be carried out according to any polymerization techniques well known to a person skilled in the art: solution polymerization, suspension polymerization, gel polymerization, precipitation polymerization, emulsion polymerization (aqueous or reverse) followed by an isolation step in order to obtain a powder, for example a spray drying step, or micellar polymerization followed by an isolation step for example a precipitation step in order to obtain a powder.

The polymerization is generally a free radical polymerization preferably by inverse emulsion polymerization or gel polymerization. By free radical polymerization, we include free radical polymerization by means of U.V. azoic, redox or thermal initiators and also Controlled Radical Polymerization (CRP) techniques or template polymerization techniques.

Dosage

In the method of the present invention, the anionic flocculant is added into the aqueous suspension of mineral particles to treat in an amount comprised between 100 and 2500 g/ ton of solids, preferably between 700 and 1500 g/ton of solids.

The cationic flocculant is added into the aqueous suspension of mineral particles to treat in an amount comprised between 50 and 1000 g/ ton of solids, preferably between 100 and 600 g/ton of solids. The cationic coagulant is added into the aqueous suspension of mineral particles to treat in an amount comprised between 25 and 1000 g/ ton of solids, preferably between 100 and 600 g/ton of solids.

Flocculant / Coagulant addition

According to the invention, the water soluble polymers are preferably added in the form of an aqueous solution. Polymers are often in powder form, sometimes in emulsion form. They are preferably prepared in concentrated solution, called "mother solution" at a concentration comprised between 0.1 and 2 weight %. A solution is prepared for each of the anionic and cationic water soluble polymer, generally by diluting the "mother solution". Then, said diluted solutions are added into the tailings in the appropriate amount and according the specific sequence of the method of the invention.

Mixing Step

The mixing step may be caused by the turbulences in the pipeline transporting the treated tailings to the centrifugation, or may be caused by inline static mixer or inline dynamic mixer.

Centrifugation Step

The tailings treated with anionic flocculant and then with cationic flocculant or cationic coagulant is pumped into the centrifuge. The mixture is spanned in a large cylindrical vessel at high speeds, typically between 1,000 and 3000 rotations per minute (rpm), the water is forced from the tailings mixture. This results in a cake of solids that may be discharge in a dedicated disposal area and recovered water that may be recycled.

In a preferred embodiment of the invention, the method for treating an aqueous suspension of mineral particles comprises sequentially:

- adding an anionic flocculant in the suspension,
- mixing the resulting treated suspension,
- adding a cationic flocculant or a cationic coagulant in the suspension,
- mixing the resulting treated suspension,
- centrifuging the resulting mixture,
- discharging the cake obtained after centrifugation in a disposal area,
- recovering the water obtained after the centrifugation step
- preparing separate aqueous solutions containing the anionic flocculant or the cationic flocculant or the cationic coagulant by adding said anionic flocculant or the cationic flocculant or the cationic coagulant in the recovered water.

According to this embodiment, the recovered water is not treated between the centrifugation step and its use in the preparation of the water soluble polymer solution.

Generally, suspensions of suspended solids or tailings are concentrated and contains between 10% and 60% solids by weight, preferably between 20 and 50% solids. But suspensions having lower solids content may be efficiently treated with the method of the invention.

The method using the composition permits to treat more efficiently mineral material, especially the suspensions having high clay content.

It has been discovered that the method according to the invention may be especially useful for the treatment of tailings resulting from oil sand extraction, such as Mature Fine Tailings (MFT).

The treatment of oil sand tailings has recently become an increasing issue in Canada. The tailings waste goes to tailings pond or thickeners for further water management. The oil sands tailings are alkaline aqueous suspensions which contain un-recovered residual bitumen, salts, soluble organic compounds, sands and clays. The tailings are discharged to tailings ponds for storage.

The tailings ponds are also closely regulated by the government. Two to four barrels of fresh water are required per barrel of oil produced from the surface mining method. After the tailings slurry is discharged to the tailings ponds, the coarse solids segregate as the dykes while most of the water and fine solids remain as suspensions in the tailings pond. A layer of mature fine tails (MFT) develops after two to three years.

MFT consolidates very slowly. The completion of the settling process is predicted to take almost a century.

The method of the invention may provide a very efficient method for treating MFT.

The dual synthetic polymer treatment outperformed the known process. It may increase cake solids, which may lead to significant reduction of tailings volume and faster reclamation of the tailings. It may increase recovered water quality. Recovered water can be recycled immediately back to a process, for example for the bitumen extraction process or for making down polymer solution. This may considerably reduce operation cost.

It also may increases robustness of the process (widen operation windows). The dual synthetic polymer treatment can be less sensitive to feed variation, maintaining good performance with wide dosage windows, mixing.

Figure 1 is a diagram showing the cake solids contents (in weight %) and the centrate clarity (recovered water quality) (in clarity wedge) with a single addition of anionic flocculant in the treatment of a MFT by centrifugation.

Figure 2 is a diagram showing the performances of a single addition compared to the dual treatment according to the invention in the treatment of a MFT by centrifugation.

Figure 3 shows pictures and table comparison of recovered water quality between single addition compared to the dual treatment according to the invention in the treatment of a MFT by centrifugation.

Obviously, the following examples are only given to illustrate the subject matter of the invention, which is in no way restricted to them.

EXAMPLE

Laboratory tests show that the dual polymer process increases tailings dewatering and decreases solids content of the recovered water.

Methodology

MFT and process water samples is obtained from Oil Sands operator. The solids content of the MFT is 24.6%.

Three polymers are used:

- anionic flocculant, AF: copolymer of acrylamide and sodium acrylate (7 /3 molar ratio) – Molecular weight of 13-14 Million daltons;
- cationic flocculant, CF: polymer of DMAEA MeCl - Molecular weight of 7-8 Millions daltons, and
- cationic coagulant, CC: PolyDADMAC – Molecular weight of 600-800 Thousand daltons.

Polymer solutions are prepared at a concentration of 0.4% by weight using process water. 200 g samples of MFT are treated either with anionic polymer alone or with anionic polymer followed by cationic polymer (flocculant or coagulant).

The flocculated samples were centrifuged using bench top centrifuge, Heraeus Megafuge 16, at 2800 rpm (g-force of 900) for 5 min after which the quantity and quality of centrate as well as solids content of the resulted cake were determined.

Results

The dosage curve for single treatment with AF in Figure 1 shows that at optimal dosage of 1600 g/t, cake solids reached 38.4% with good centrate of clarity wedge of 13. Higher dosage increases centrate quality but reduces cake solids.

Comparison between single and dual polymer treatment in Figure 2 shows that dosage of single treatment was 1600 g/t of AF and for dual polymer, it was 1600 g/t for AF and 400 g/t for cationic polymers (either CF or CC). The dual treatment according to the invention increases cake solids to 44 wt.% as compared to 38 wt.% for single anionic treatment. Dual treatment also produced very clean centrate with negligible total suspended solids (TSS). For single treatment, TSS was 0.02 wt.%. This indicates that dual polymer treatment significantly improved centrifugation over single treatment.

As shown in Figure 1, additional anionic flocculant didn't increase performance. When dosage is increased from 1600 g/t to 1800 g/t cake solids content decreases by 2 wt%.

It means that dewatering performance cannot be improved with increasing the dosage of single anionic polymer. However, the performance can be enhanced with an additional cationic polymer as used in the method according to the invention.

Images of process water and centrate from single and dual polymer treatments along with TS and TSS in Figure 3 show that dual polymer treatment improved significantly centrate quality, giving negligible TSS. This water can be recycled immediately to centrifugation process as make-down water.

CLAIMS

1. Method for treating an aqueous suspension of mineral particles comprising sequentially:

- adding an anionic flocculant in the suspension,
- mixing the resulting treated suspension,
- adding a cationic coagulant having a molecular weight less than 1 million daltons in the suspension,
- mixing the resulting treated suspension,
- centrifuging the resulting mixture.

2. The method according to claim 1, wherein the anionic flocculant is a synthetic water soluble polymer having an anionicity ranging from 10 to 70 mol%.

3. The method according to claim 1 or 2, wherein the cationic coagulant is a synthetic water soluble polymer having a cationicity of 100 mol%.

4. The method according to any one of claims 1 to 3, wherein the anionic flocculant is added into the aqueous suspension of mineral particles to treat in an amount comprised between 100 and 2500 g/ ton of solids.

5. The method according to any one of claims 1 to 4, wherein the cationic coagulant is added into the aqueous suspension of mineral particles to treat in an amount comprised between 25 and 1000 g/ ton of solids.

6. The method according to any one of claims 1 to 5, wherein said method further comprising:

- discharging a cake obtained after centrifugation in a disposal area,
- recovering water obtained after the centrifugation step,
- preparing separate aqueous solutions containing the anionic flocculant or the cationic coagulant by adding said anionic flocculant or the cationic flocculant or the cationic coagulant in the recovered water.

7. The method according to any one of claims 1 to 6, wherein the aqueous suspension of mineral particles has a concentration of solids comprised between 10% and 60% solids by weight.

8. The method according to any one of claims 1 to 7, wherein the aqueous suspension of

Date Reçue/Date Received 2022-10-19

mineral particles is a tailings resulting from oil sand extraction.

9. The method according to any one of claims 1 to 8, wherein the aqueous suspension of mineral particles is a Mature Fine Tailings.

Date Reçue/Date Received 2022-10-19

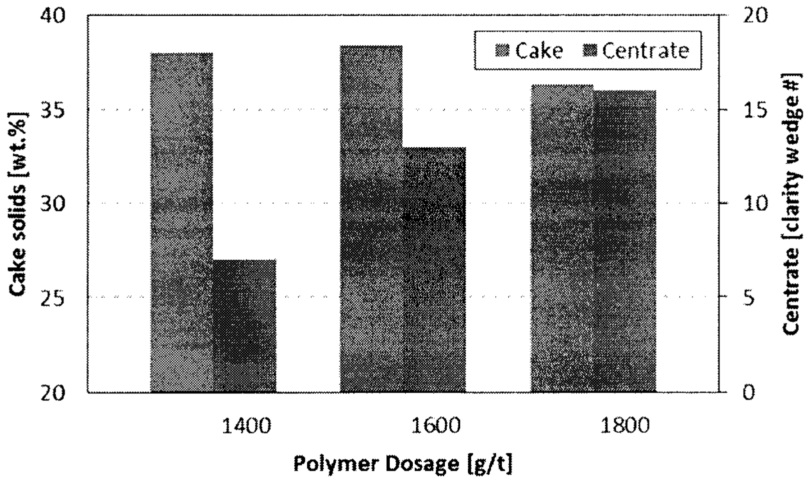


Figure 1: Solids content of centrifuge cake vs. anionic polymer (AF) dosage

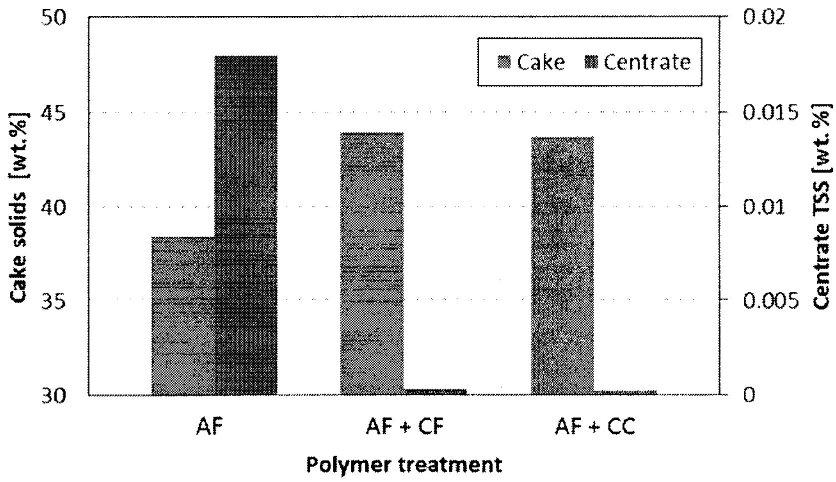
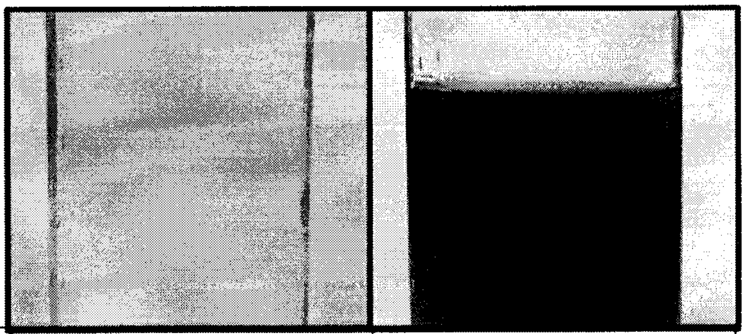
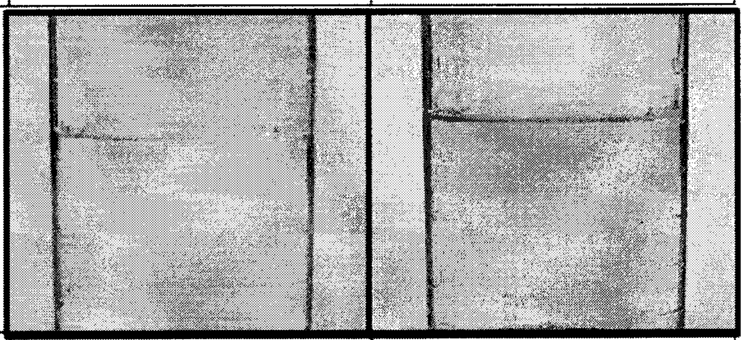


Figure 2: Single vs. dual polymer treatment

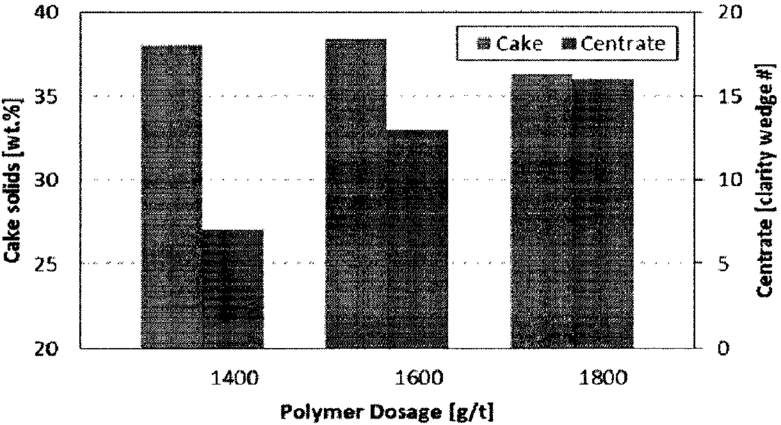


Water/Centrate	Process water	AF treatment
Total solids [wt.%]	0.054	0.115
Total suspended solids [wt.%]	0.0052	0.018



Water/Centrate	AF + CF	AF + CC
Total solids [wt.%]	0.096	0.099
Total suspended solids [wt.%]	0.0002	0.0003

Figure 3: process water and centrate from single and dual polymer treatments along with TS and TSS



Solids content of centrifuge cake vs. anionic polymer (AF) dosage