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(54) Titre : POLYMERES REDUCTEURS DE FRICTION DESTINES AU TRANSPORT D'EAU DE TRAITEMENT RECYCLEE DANS LES PROCEDES DE RECUPERATION DE SABLES BITUMINEUX

(54) Title: FRICTION REDUCERS POLYMERS FOR THE TRANSPORTATION OF RECYCLED PROCESS WATER IN OIL SAND RECOVERY PROCESS

(57) Abrégé/Abstract:
A process for oil sand recovery comprising adding a friction reducer to the process water, and then recycling the process water into the said process, wherein, the said friction reducer comprises a water soluble polymer having a molecular weight over 1 million Dalton comprising:
- at least one non-ionic monomer;
- at least one anionic monomer containing a sulfonic acid moiety or its water soluble salts,
wherein the total content of anionic monomers in the polymer is comprised between 10 mol% and 70 mol%.

ABSTRACT

A process for oil sand recovery comprising adding a friction reducer to the process water, and then recycling the process water into the said process, wherein, the said friction reducer comprises a water soluble polymer having a molecular weight over 1 million Dalton comprising:

- at least one non-ionic monomer;
- at least one anionic monomer containing a sulfonic acid moiety or its water soluble salts,

wherein the total content of anionic monomers in the polymer is comprised between 10 mol% and 70 mol%.

FRICTION REDUCERS POLYMERS FOR THE TRANSPORTATION OF RECYCLED PROCESS WATER IN OIL SAND RECOVERY PROCESS

TECHNICAL FIELD OF THE INVENTION

The invention relates to the use of a specific polymer as friction reducer for the transportation of process water coming from oil sands processes and intended to be recycled in the said processes.

BACKGROUND

Oil sands, also known as tar sands or bitumen sands, are one of the world's largest sources of crude oil. The vast majority of the world's oil sands reserves is located in North America, in particular Canada, with some further reserves in South America. Generally, an oil sand recovery process includes at least the following steps:

- Surface oil sand is mined from the ground and transported to a crushing facility,
- Once oil sands ore is crushed for size reduction, hot water is added to the mixture to form a slurry containing sand, clay, bitumen and water that can be pumped to the extraction plant,
- At the extraction plant, the slurry is introduced in a large separation vessel within which additional hot water is added and a settling time is provided to allow the slurry components to separate, this step is called primary separation step. As the slurry settles, bitumen froth rises to the surface and sediments (rocks, clay, and sand) settle to the bottom of the separation vessel. The bottom layer containing sand, clays and traces of bitumen is then directed to settling ponds, while the middle layer is removed for further bitumen recovery,
- Bitumen is recovered from the middle layer by applying at least two additional successive flotation (primary flotation and secondary flotation) steps wherein air is bubbled into the suspension, the bitumen droplets become attached to air bubbles and float to the top of the vessel allowing most of the bitumen to be recovered as a product called bitumen froth and, like in the

primary separation step, the bottom layers coming from primary flotation and secondary flotation and containing clays and small quantities of bitumen are directed to settling ponds.

So, after the primary separation and flotation steps, a mixture of clays, water, sand and traces of bitumen combined with process chemicals, known as tailings is pumped out to settling ponds.

The settling ponds or large containment dykes are also known as tailing ponds. A significant portion of water released to tailing ponds can be recycled. However the residual tailings mixture remains indefinitely. Any water from tailing ponds cannot be released to the environment without undergoing further treatment.

The water which is recovered from the oil sands activity is commonly named "process water". It is advantageously used as recycling water. Since only 3% of the Athabasca river is allocated to existing and future oil sands mining operations, this process water is highly valuable for the oil sands companies. It can be recovered after bitumen extraction in primary separation and flotation vessels, but also from oil sand tailings after a dewatering treatment of these latter, using techniques (centrifugation, thickeners, dry-stacking, beach deposition...) and chemicals (flocculants, coagulants, dispersants...), known by the skilled man.

TECHNICAL PROBLEM SOLVING

When the process water is recycled, it has to be transported in very long pipes across oil sand extraction installation. This process water contains small quantities of clays (typically, between 0.1 and 0.5 wt%). In order to have high water flow rate and to minimize energy needs for water transportation, water soluble friction reducers are added. Acrylamide and acrylic acid (and their salts) copolymers are good water soluble friction reducers commonly used. However, it appears that these polymers disturb the different steps of the oil sand recovery process (primary separation, flotation steps and final settling step (in tailing pond)) when the process water which is recycled in the oil sand process is treated with such friction reducers.

DESCRIPTION OF THE INVENTION

The applicant has found that the use of specific polymers as friction reducers for the transportation of the process water does not affect the efficiency of the primary separation, flotation steps and final settling step when said process water is recycled in the oil sand recovery process.

In the present invention, the use of a friction reducer consisting of a total or partial substitution of monomers containing at least one carboxylic acid moiety, or its water soluble salts by anionic monomers containing a sulfonic acid moiety, or its water soluble salts, in copolymers of (meth) acrylamide and monomers containing at least one carboxylic acid moiety, or its water soluble salts, allow to solve the problem previously described.

The invention concerns a process for oil sand recovery comprising adding a friction reducer to the process water, and then recycling the process water into the said process, wherein the said friction reducer comprises, advantageously consists of a water soluble polymer having a molecular weight over 1 million Dalton comprising:

- at least one non-ionic monomer;
- at least one anionic monomer containing a sulfonic acid moiety or its water soluble salts,

wherein the total content of anionic monomers in the polymer is comprised between 10 mol% and 70 mol%.

In a preferred embodiment:

- the non-ionic monomer is chosen from the group consisting of (meth)acrylamide and its non-ionic derivatives, N-vinyl acetamide, N-vinyl formamide, N-vinylpyrrolidone, N-vinyl acetate;

- the monomer with a sulfonic acid moiety is chosen from the group consisting of 2-acrylamido-2-propanesulfonic, vinylsulfonic, allylsulfonic, styrenesulfonic acids and their water soluble salts.

Preferably, the water soluble polymer comprises at least one anionic monomer containing at least a carboxylic acid moiety or its water soluble salts.

Preferably, the monomer with at least one carboxylic acid moiety is chosen from the group consisting of (meth)acrylic, itaconic, fumaric and maleic acids and their water soluble salts.

Advantageously, the water soluble salts of anionic monomers, with carboxylic acid or sulfonic acid moieties, are typically salts of an alkali metal, an alkaline earth metal or ammonium and preferably salt of sodium.

The total content of anionic monomers in the polymer is comprised between 10 and 70 mol%, but advantageously it is comprised between 20 and 60 mol% and more advantageously between 30 and 50 mol%.

The polymer of the invention contains at least one non-ionic monomer. Preferably, the polymer contains between 30 and 90 mol% of non-ionic monomers.

More preferably:

- the non-ionic monomer is (meth)acrylamide;
- the monomer with at least one carboxylic acid moiety is (meth)acrylic acid or its water soluble salts;
- the monomer with a sulfonic acid moiety is 2-acrylamido-2-propanesulfonic acid or its water soluble salts.

To have an effective friction reducer effect, the concentration of friction reducer in the process water is preferably comprised between 10 ppm and 200 ppm.

The process water intended to be recycled could be recovered from a primary separation step, a flotation step or a settling step or a dewatering step (with/or without a chemical agent by centrifugation, thickeners, dry-stacking, beach deposition), all this steps being involved in an oil sand recovery process.

Preferably, the process water intended to be recycled corresponds to the supernatant present in the tailing ponds after the settling step.

In one embodiment, the friction reducer according to the invention is added to the process water intended to be recycled after the settling step.

Advantageously, the process water containing the friction reducer is recycled and mixed with fresh water before being used in the process for oil sand recovery.

The process water containing the friction reducer according to the invention could be recycled in any step of the process which needs water. Preferably, the process water containing the water soluble polymer is recycled in the step of primary separation, of flotation, of oil sand slurry preparation, of dissolution of chemicals used for dewatering or of tailings dilution.

Further examples and counter examples, highlight that the use of polymers according to the invention, as friction reducers, allow to recycle water coming from oil sand recovery process without disturbing primary separation step, flotation steps and final settling step (in tailing pond) of oil sand recovery process.

<u>Example 1: Flocculation tests into oil sand recovery process water</u>

Several polyacrylamide-based polymers, with various contents of anionic monomers, have been prepared by the gel polymerization method. Their molecular weights are over 1 million Dalton. Polymers were poured into distilled water to provide aqueous solutions at concentrations of 0.1 wt%. All solutions were mechanically stirred at 500 rpm until complete dissolution to obtain clear and homogeneous polymer solutions.

Flocculation tests have been performed using oil sand recovery process water obtained from an oil sands mining site in the Athabasca region. For each test, the appropriate volume of polymer solution was added into 200 mL of process water and then the whole mixture was mechanically stirred at 500 rpm during 1 min.

Results displayed in Table 1 show that all polymers with a content of anionic monomers lower than 20 mol% and higher than 50 mol% induce flocculation of the particles suspended into process water, especially those with a content of anionic monomers lower than 10 mol%. Since the flocculation process consumes polymers and could potentially lead to solid accumulation into the pipelines during process water transportation, it is highly desirable to avoid it. According to data disclosed into Table 1, polymers with a content of anionic monomers comprised between 30 mol% and 50 mol% do not lead to any visible flocculation.

Table 1. AM = acrylamide ; AA = sodium acrylate ; AMPS = 2-Acrylamido-2-methylpropane sulfonic acid

		Polymer dosage in process water		
Polymer	AM/AA/AMPS mol%	25 ppm	50 ppm	100 ppm
A	100/0/0	+++	+++	+++
B	95/5/0	+	++	++
C	90/10/0	+	++	++
D	87/13/0	-	-	-
E	74/26/0	0	-	-
F	70/30/0	0	0	0
G	50/50/0	0	0	0
H	40/60/0	-	-	-
I	30/70/0	-	-	-
J	10/90/0	-	-	-

K	5/95/0	-	-	-
L	0/100/0	-	-	-
M	95/0/5	+	++	++
N	85/0/15	0	0	0
O	70/0/30	0	0	0
P	68/0/32	0	0	0
Q	50/0/50	-	-	-
R	30/0/70	-	-	-
S	20/0/80	-	-	-
T	0/0/100	-	-	-
U	75/20/5	0	0	0
V	70/15/15	0	0	0
W	60/20/20	0	0	0

0 = no visible flocculation

- = bad flocculation

+ = weak flocculation

++ = good flocculation

+++ = very good flocculation

<u>Example 2: Shear stability tests</u>

Some of the previously described polymers were poured into oil sand recovery process water to provide aqueous polymer solutions at concentrations of 0.5 wt%. All solutions were mechanically stirred at 500 rpm until complete dissolution in order to obtain homogeneous polymer solutions.

For each test, the appropriate volume of polymer solution was added into 2 L of oil sand recovery process water and shear stability tests have been performed using oil sand recovery process water in turbulent flow using a flow loop. A 6 meters pipe with a diameter of 4.57 mm has been used. At 20°C and at a 340 L/h flow rate, the applied Reynolds number is 30000.

Results displayed in Table 2 show that polymers with a content of anionic monomers higher than 70 mol% are extremely sensitive to shear degradation and cannot be used as friction reducer.

Table 2.

Polymer	AM/AA/AMPS mol%	Shear stability after 5 min
D	87/13/0	Medium stability
F	70/30/0	Good stability
H	40/60/0	Good stability
I	30/70/0	Poor stability
L	0/100/0	Very poor stability
N	85/0/15	Medium stability
O	70/0/30	Good stability
S	20/0/80	Poor stability
T	0/0/100	Poor stability
V	70/15/15	Good stability

<u>Example 3: Impact of friction reducer on bitumen recovery</u>

Previous process water samples obtained after shear resistance tests (i.e. samples of process water containing friction reducer) were then used to check if the presence of friction reducer has an impact on bitumen recovery during the aqueous flotation process currently in place to recover bitumen from Canadian Oil Sands. A sample of medium-grade oil sand (Alberta Innovates Technology Futures, Edmonton, Canada) was used for these tests. It is composed of 85.05 % of solids (clay + sand), 11.26% of bitumen and 3.69 % of water. These values are expressed as weight percentages and are determined by extraction with toluene using a Dean-Stark apparatus. A primary separation step and a flotation step were conducted in a laboratory scale Batch Extraction Unit flotation cell (Alberta Innovates, Alberta, Canada) following the original Syncrude protocol described hereinafter.

1/ Conditioning step:

500 g of oil sand and 150 g of recycled process water at 40°C are poured into a 2 L rectangular double-layer steel tank. The temperature is kept constant at 40°C throughout the experiment by continuous circulation of a hot water bath through the tank. The mixture of process water and oil sand is left under these conditions for 1 min. This mixture is then stirred at 600 revolutions/min for 10 min under a continuous air stream of 420 mL/min.

2/ Primary separation step:

After the conditioning step, 1000 g of recycled process water at 40°C are added to the tank and the air stream is stopped. The stirring of the medium is maintained at 600 revolutions/min for 10 min, during which the bitumen froth formed is recovered in a beaker. Once the stirring has stopped, all the bitumen froth is recovered.

3/ Flotation step:

The stirring at 780 revolutions/min begins again and is maintained for 5 min under an air stream of 234 mL/min. At the end of this step, all the bitumen froth formed is recovered.

The weight ratios of bitumen for each fraction (froths from the primary separation step and the flotation step) are determined by extraction with toluene using Dean-Stark apparatuses. One can see from Table 3 that copolymer F (70 mol% AM+ 30 mol% AA) leads to a 6% decrease in bitumen extraction yield whereas copolymer O (70 mol% AM + 30 mol% AMPS) and terpolymer V (70 mol% AM + 15 mol% AA + 15 mol% AMPS) do not impact the bitumen extraction yield.

Table 3.

Additive in the process water	Dosage (mg/kg)	Bitumen extraction yield (%)		
		Primary separation step	Flotation step	Total (primary separation step + flotation step)
None 1	-	41.9	36.7	78.6
None 2	-	38.2	39.6	77.8
None 3	-	42.6	37.9	80.5
Polymer F	100	34.7	37.0	71.7
Polymer O	100	44.6	33.1	77.7
Polymer V	100	38.7	38.9	77.6

Example 4: Impact on clay sedimentation

After bitumen recovery (cf example 3), the residual tailings have been collected and let to rest 7 days to check if the presence of friction reducer in the process water has an impact on clays sedimentation. When no friction reducer is present in the process water used for oil sands flotation, the aqueous phase obtained has a turbidity of 89 FAU (Formazin Attenuation Unit). As evidenced in Table 4, turbidity measurements of the upper aqueous layer of the tailings, after resting, show that copolymer F significantly prevents the natural sedimentation of the clays. This polymer seems to exert a dispersing effect which decreases the water quality. As this water will be reinjected back into the process and be used as process water, it has to be as clean as possible. Polymers O and V have no visible impact on clays sedimentation.

Table 4.

Dosage in process water (mg / kg)	25	50	100
Polymer F	2100	2205	2451
Polymer O	89	87	105
Polymer V	120	102	80

Example 5: Oil Sands Mature Fine Tailings dewatering tests

It is necessary to check if the presence of friction reducer in the process water used to prepare flocculant solutions has an impact on the flocculating properties of these latters. The flocculant used is a 30 mol% anionic polyacrylamide with a high molecular weight (over 1 million Daltons). The flocculant is stirred into oil sands process water containing friction reducer to provide aqueous solutions at concentrations of 0.4 wt% of flocculant. All solutions were mechanically stirred at 500 rpm until complete dissolution to obtain homogeneous solutions. Flocculation tests have been performed using Mature Fine Tailings (MFT) from a tailing pond with solid content of 42.4 wt%. For each test, the appropriate volume of flocculant solution was added into 200 g of MFT and then, the whole mixture was mixed manually until flocculation and water release were observed.

Results displayed in Table 5 show that the presence of polymers F, O or V has no visible impact on the flocculant efficiency. None of these friction reducer impacts neither the flocculant dosage nor its dewatering performances.

Table 5.

Dosage in process water (mg / kg)	Optimum flocculant dosage (g / dry tonne)	24h NWR[a]
None	955	7.2 %
100 mg/kg Polymer F	955	7.8 %
100 mg/kg Polymer O	955	6.4 %
100 mg/kg Polymer V	955	7.4 %

[a]: NWR = Net Water Release. It corresponds to the total amount of water recovered during the flocculation test.

CLAIMS

1. A process for oil sand recovery comprising adding a friction reducer to process water, and then recycling the process water into the said process, wherein the said friction reducer comprises a water soluble polymer having a molecular weight over 1 million Dalton comprising:
- at least one non-ionic monomer; and
- at least one anionic monomer containing a sulfonic acid moiety or its water soluble salts,

wherein the total content of anionic monomers in the polymer is comprised between 10 mol% and 70 mol%.

2. The process according to claim 1, wherein:
- the non-ionic monomer is chosen from the group consisting of (meth)acrylamide and its non-ionic derivatives, N-vinyl acetamide, N-vinyl formamide, N-vinylpyrrolidone and N-vinyl acetate; and
- the monomer with a sulfonic acid moiety is chosen from the group consisting of 2-acrylamido-2-propanesulfonic, vinylsulfonic, allylsulfonic, styrenesulfonic acids and their water soluble salts.

3. The process according to claim 1 or 2, wherein the water soluble polymer comprises at least one anionic monomer containing at least a carboxylic acid moiety or its water soluble salts.

4. The process according to claim 3, wherein the monomer with at least one carboxylic acid moiety is chosen from the group consisting of (meth)acrylic, itaconic, fumaric and maleic acids and their water soluble salts.

5. The process according to any one of claims 1 to 4, wherein the polymer contains between 30 and 90 mol % of non-ionic monomers.

6. The process according to claim 3, wherein:
- the non-ionic monomer is (meth)acrylamide;

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- the monomer with at least one carboxylic acid moiety is (meth)acrylic acid or its water soluble salts; and
- the monomer with a sulfonic acid moiety is 2-acrylamido-2-propanesulfonic acid or its water soluble salts.

7. The process according to any one of claims 1 to 6, wherein the friction reducer concentration in the process water is comprised between 10 and 200 ppm.

8. The process according to any one of claims 1 to 7, wherein the process water containing the friction reducer is recycled in any step of the process which needs water.

9. The process according to claim 8, wherein the step is a primary separation, a flotation, an oil sand slurry preparation, a dissolution of chemicals used for dewatering or a tailings dilution.

10. The process according to any one of claims 1 to 9, wherein the process water corresponds to the supernatant present in tailing ponds after a settling step.

11. The process according to any one of claims 1 to 10, wherein the friction reducer is added to the process water, after a settling step.

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