TREATMENT OF OILFIELD PRODUCED WATER: A CLEANER PROCESS FOR PRODUCING SODIUM CARBONATE (SODA ASH)

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ABSTRACT

The objective of this research was to obtain soda ash from oilfield produced water. The association between produced water and the conditions to produce soda ash, its processes and reactions, inspired the development of this innovative research. With the goal of transforming this wastewater in a high value product, this research performed and compared different treatment processes. An anionic surfactant was used in the flotation process of the dispersed oil phase, and sodium carbonate was employed to promote calcium and magnesium precipitations. The relationship between the liquid effluents and solid wastes with the quality of the soda ash produced was established. The quality parameters for treated water were determined, and the different streams derived from these treatments were used in the production of soda ash. The soda ash obtained in this research presented physicochemical composition similar to the one of a carbonate mineral (trona ore). The yields were as high as 80%. This process allowed to treat and to transform produced water, an effluent that is harmful to the environment, into soda ash which is largely used in the industry.

KEYWORDS

produced water; soda ash; wastewater treatment; surfactant; flotation

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1. INTRODUCTION

The petroleum production is associated to the water production. The amount of generated water can either derive from the reservoir itself or is a result of the water injection processes, and is referred to as produced water, PW. The volume of produced water in a depleted oil well can exceed 70%. This water contains high salinity levels and many polluting substances, such as heavy metals and petroleum itself (Tellez et al., 2002). Currently, due to environmental concerns and as a result of imposition of pollutant-concentration limits by the environmental laws (CONAMA, 2007; 2011), the development of processes and/or technologies to treat these waters is set of priority. As a result, many works have been performed, not only with the intention of removing the oil from the produced water (Ahmadun et al., 2009; Wu et al., 2008; Bande et al., 2008; Mostefa and Tir, 2004), but also with the objective of treating it and finding adequate solutions to its disposal (Middleditch, 1984; Al-Hubail and El-Dash, 2006).

The Solvay process was developed by Ernest Solvay in 1860. It consists of the reaction of sodium chloride with calcium carbonate to produce soda ash. This reaction does not happen in a single stage, but in a sequence of reactions under industrial conditions, according to the following description (May and Rudd, 1976):

The reactions presented in Equations 1 to 6 describe the process from the carbon dioxide generation stage to the sodium bicarbonate thermal degradation, to form the soda ash. In this process, there is a production of ammonia and carbon dioxide which, when mixed with the aqueous solution of sodium chloride, promote sodium bicarbonate precipitation (Araújo et al., 1998).

The association between the characteristics of

produced water and the conditions to obtain the soda ash, considering its processes and reactions, inspired the development of this research. The main raw material in the Solvay process is the sodium chloride and the produced water, which contains high levels of this salt. The use of this wastewater as the base in the soda ash production appears as an opportunity to direct this water to an economically viable destination. As a result, the region where petroleum is produced will profit both from the generation of extra income and mitigation of environmental problems. As mentioned earlier, produced water represents a problem for the petroleum industry, due to its high volume and to the lack of technology for treating it in a fast and effective way.

Advances in the search of novel ways to use produced water enable not only their proper treatment, but also provide new sources of raw materials that may be important to industries. In light of this context, the objective of this work is to achieve soda ash from produced water. It also seeks to understand how different kinds of treatment techniques performed in the produced water affect the quality of the soda ash obtained, considering liquid and solid streams generated during the process.

2. MATERIALS AND METHODS

2.1 Materials

The experiments were carried out with two distinct samples of produced water: one obtained prior to the flotation process, referred as produced water (PW), and another collected after the flotation process (FPW). PW and FPW were used as supplied by Petrobras (Table 1).

The anionic surfactant used in this research was derived from coconut oil. The surfactant synthesis is well described in a previous work (Castro Dantas et al., 2003). Sodium carbonate (soda ash) was supplied by VETEC (99.5% purity).

2.2 Produced water treatments

The produced water treatments were accomplished according to the flowchart shown in Figure 1. Analyzing the flowchart, one can observe the formation of different aqueous streams that

Table 1. Characterization of PW and FPW.

Parameters	PW	FPW
pH	7.32	6.89
Turbidity, NTU	472.0	41.3
OD, mg O ₂ /L	1.3	3.5
Conductivity, mS/cm	57.9	55.4
Cl ⁻ , g/L	34	33
Na, g/L	22.4	21.7
K, mg/L	240	260
Mg, mg/L	730	705
Ca, mg/L	2,500	2,400
Fe, mg/L	15	2
Mn, mg/L	2.2	2.0
Zn, mg/L	1.2	1.2
B, mg/L	20	15
Ba, mg/L	12	7
H ₂ S, mg/L	250	5

will comprise part of the input material in the soda ash formation process, where: SPW is the produced water treated with surfactant; SCPW is the produced water treated with sodium carbonate; SFPW is the produced water after flotation cell, using surfactant as additive; and SCFPW is the produced water after flotation cell, using sodium carbonate as additive.

2.2.1 PW and FPW treatment using an anionic surfactant

The oil was removed from the produced water (PW) and the floated produced water (FPW) using an anionic surfactant, followed by froth flotation in a glass column (4.8-cm inner diameter by 93-cm height) with an air injection flow rate of 700mL/min. The surfactant was added to PW and FPW as an aqueous solution to adjust the surfactant concentration to 2g/L, under agitation, promoting flake formation (surfactant+oil). Later, the solution was submitted to the flotation (Lima et al., 2008), generating the produced water streams SPW and SFPW.

To determine the oil concentration in the treated aqueous phase, a 5-mL sample was collected. Subsequently, the sample was mixed with 5mL of chloroform, under agitation, for 5 minutes. Then, it was submitted to centrifugation under 4,000 rpm. The chloroform phase was analyzed in a molecular absorption spectrophotometer at a 260nm⁻¹ wavelength (λ).

2.2.2 PW and FPW treatment using soda ash

Metallic calcium and magnesium were removed as carbonates by adding soda ash. The soda ash was added to PW and FPW, under agitation, until

Figure 1. The flowchart of the produced water treatment using sodium carbonate (soda ash) and surfactant.

Table 2. Methods used in the evaluation of the streams obtained during the soda ash production.

Parameter	Standard/ Equipment
pH	pH meter Tecnal Tec 370
Turbidity, NTU	Molecular absorption spectrophotometer Varian Cary 50 Conc with reference of standard solution of formazine in 400 NTU
OD, mg O ₂ /L	Dissolved Oxygen Instrument (YSI Inc, Model : 5100)
Conductivity, mS/cm	Conductivimeter (Digimed Inc, model DM-32)
Cl ⁻ , g/L	Mohr method
Na, K, Mg, Ca, Fe, Mn, Zn, B, Ba, Cr, Ni, Cu, Cd, Ag, Pb, Hg	Atomic absorption spectrophotometer Varian – Model AA240 Method detection limit (0.1 mg/L)

reaching a concentration of 1,000mg/L. After 5 minutes, the solids were filtered out and the aqueous phases SCPW and SCFPW were obtained. The analysis of these streams was done using the methods showed in Table 2.

2.3 Soda ash obtaining process

The process of obtaining soda ash from produced water was performed according to Figure 2. The average concentration of sodium chloride in

the produced water used in this work was around 5.5%. In the Solvay process, it is necessary to feed the reactor with solutions which have sodium chloride concentration at the saturation point. Before the reaction, the aqueous phases (SPW, SCPW, SFPW, and SCFPW) were evaporated in a hot plate (110°C) to concentrate the water until the saturation point. After evaporation, the concentrated aqueous phases were used to feed the reactor.

Figure 2. Flowchart of the soda ash production process.

Table 3. Nomenclature adopted to describe the streams in soda ash production process.

Stream name	Abbreviation
Ammonium chloride solution obtained from SCPW	ASC
Ammonium chloride solution obtained from SPW	AS
Ammonium chloride solution obtained from SFPW	ASF
Ammonium chloride solution obtained from SCFPW	ASCF
Bicarbonate obtained from SCPW	BSC
Bicarbonate obtained from SPW	BS
Bicarbonate obtained from SFPW	BSF
Bicarbonate obtained from SCFPW	BSCF
Carbonate obtained from SCPW	CSC
Carbonate obtained from SPW	CS
Carbonate obtained from SFPW	CSF
Carbonate obtained from SCFPW	CSCF

The reactor operated in a batch regime and it was fed with a mixture of 70 wt % of aqueous phase and 30 wt % of ammonium hydroxide. Then, carbon dioxide was injected until the pH reached 7.5. This pH value corresponds to the condition under which most carbonate ions in the aqueous phase appear as bicarbonates (Soli and Byrne, 2002). A thermostatic bath was used to maintain the system at 16°C.

Figure 2 shows many input and output streams in the soda ash production process. Table 3 shows the nomenclature adopted for these streams. Among these streams there was a liquid phase generated in the reactor that corresponds to the filtered phase, which was rich in ammonium chloride (AS, ASF, ASC, and ASCF). There was also a solid phase produced in the reactor and retained in the filter, which corresponds to the precipitate sodium bicarbonate (BS, BSF, BSC, and BSCF). This precipitate was, later, submitted to thermal decomposition producing the soda ash (CS, CSF, CSC, and CSCF). The stage of bicarbonate thermal decomposition was performed in an oven, under 200°C. This stage corresponds to the reaction showed in equation (6), obtaining the soda ash (sodium carbonate).

3. RESULTS AND DISCUSSION

3.1 Produced water treatment

The anionic surfactant used in the treatment of the produced waters (PW and FPW) has, as a premise, the ability to reduce the oil/water

interfacial tension until the point where the liquid film around the dispersed oil droplets is broken. This breakage promotes an increase in the size of these droplets, improving the flotation separation (Lima et al., 2008). This work used the flotation method to separate the flakes from the clarified wastewater, obtaining a residual concentration of oil lower than 1.0mg/L.

The results of the physicochemical analysis of the PW and FPW treated with the surfactant (SPW and SFPW) and with the soda ash (SCPW and SCFPW) are shown in Table 4. In addition to the metals displayed in the Table 4, chromium, nickel, copper, cadmium, silver, mercury, and lead were searched for, but they were not detected.

Table 4 shows that pH values are close to neutrality and an occurrence of a small increase in pH was observed when either the soda ash or the surfactant was added. This increase in pH was due to the alkalinity of these two additives.

In the turbidity study, it was observed that the PW suffered a significant decrease in its turbidity. Produced water turbidity can be generated by dispersed oil or by the presence of insoluble salts in suspension. This reduction was observed not only when PW was the input stream of a flotation process, thereby generating the FPW effluent, but also after addition of soda ash (SCPW and SCFPW) and surfactant (SPW and SFPW). By performing the flotation of the raw produced water, the turbidity decreased from 472 to 41.6 NTU. In the treatment of produced water (PW) with surfactant (SPW) and soda ash (SCPW), the turbidity was reduced from 472 to 6.9 and to 14.5 NTU, respectively. This result

Table 4. Physicochemical analyses of produced water streams treated with surfactant and with soda ash.

Parameter	PW	SPW	SCPW	FPW	SFPW	SCFPW
pH	7.32	7.76	7.40	6.89	7.60	7.85
Turbidity, NTU	472	6.9	14.5	41.3	9.2	8.3
OD, mg O ₂ /L	1.3	1.5	1.1	3.5	1.8	3.2
Conductivity, mS/cm	57.9	57.5	56.5	55.4	54.6	58.4
Cl ⁻ , g/L	34	37	38	33	32	34
Na, g/L	22.4	22.1	28.6	21.7	24.5	27.6
K, mg/L	240	270	240	260	230	240
Mg, mg/L	730	730	230	705	705	250
Ca, mg/L	2,500	2,400	15	2,400	2,300	16
Fe, mg/L	15	1.5	1.5	2	2	2
Mn, mg/L	2.2	1.6	1.6	2	1.6	0.3
Zn, mg/L	1.2	1.1	1.1	1.2	1.2	0.6
B, mg/L	20	8	8	15	8	8
Ba, mg/L	12	6	5	7	8	7
H ₂ S, mg/L	250	5	32	5	3	5

confirms the efficiency of using this surfactant treatment process. Despite the decrease in turbidity presented in the soda ash process, this reduction may be an effect of the filtration step carried out in the SCPW stream, which improved the efficiency in the removal of suspense particles. For the produced water after the flotation process (FPW), the turbidity decreased from 41.6 to 9.2 (SFPW) and to 8.3 NTU (SCFPW), respectively. In both treatments, the turbidity was reduced, either by dispersed oil flotation or by carbonate precipitation, dragging the solid particles in suspension.

The results for dissolved oxygen (OD) indicate that both the surfactant and the soda ash treatment maintain the OD values observed in PW and FPW. However, the streams that passed through the flotation cell showed an OD increase of about 100%. This result can be explained by the flotation process itself, which enhances the absorption of oxygen by water.

Despite the existence of a direct relationship between the surfactant and the soda ash with the aqueous medium's conductivity, significant variations of this propriety were not observed after the treatment. This occurred because they were added in such low concentrations that did not affect this propriety. Nevertheless, an increase in sodium concentrations was observed in samples treated with soda ash.

The calcium concentration, initially around

2,400mg/L (PW and FPW), was decreased to 15mg/L (SCPW) and 16mg/L (SCFPW) after the soda ash treatment. These numbers suggest that the soda ash is a good agent in the calcium precipitation process. For magnesium, after soda ash treatment, a decrease from 730mg/L (PW) to 230mg/L (SCPW) and 705mg/L (FPW) to 250mg/L (SCFPW) was observed, probably due to the higher solubility of the magnesium carbonate in PW and FPW.

The iron concentration was decreased from 15 ppm to, approximately, 2mg/L in both treatments, surfactant and soda ash. Considering the relation with the surfactant, the removal was due to the interaction between the iron and the surfactant anion (head group), promoting the flocculation. Considering the soda ash, it prompted iron precipitation in the form of iron hydroxide.

The barium concentration was decreased to, approximately, 50%, in both treatments. The soda ash promoted barium carbonate precipitation. In the surfactant addition, the barium interacted with the surfactant anion, forming an insoluble complex.

As far as the surfactant treatment is concerned, analysis of H₂S showed a significant decrease in its concentration (higher than 98%), which was probably due to its lipophilic character, thereby favoring interactions with the surfactant hydrophobic tail group. The soda ash treatment was less efficient than the surfactant one, with the H₂S concentration decreased by 85%. This

Table 5. Aqueous phases used to produce soda ash.

Aqueous phase	SPW	SCPW	SFPW	SCFPW
Initial aqueous phase mass (g)	3,000	3,000	3,000	3,000
Initial salt concentration (%)	6.36	6.85	6.08	6.36
Aqueous phase added to the reactor (g)	690.0	627.3	699.8	703.8
Salt concentration after evaporation (%)	24.3	21.7	25.8	19.7
Initial ammonium solution mass in the reactor (g)	312.0	313.1	373.1	288.5
Obtained bicarbonate mass (g)	462.6	469.5	462.2	429.9
Obtained ammonium solution mass (g)	603.8	664.6	717.0	648.2

Table 6. Physicochemical properties of the streams rich in ammonium chloride obtained in the reactor.

Parameter	ASC	AS	ASF	ASCF
pH	8.23	8.21	8.27	8.29
Conductivity	140	137	140	164
Turbidity, NTU	26.6	27.2	23.9	18.2
Cl ⁻ , g/L	98	104	109	83
HCO ₃ ⁻ , g/L	93	78	78	99
CO ₃ ⁼ , g/L	0.9	0.78	0.78	0.96
NH ₄ ⁺ , g/L	50	64	61	65
NH ₃ , g/L	5.1	6	6	6.8
Na, g/L	16.2	21.4	26.7	14.8
K, mg/L	620	700	700	560
Ca, Mg, mg/L	83	96	102	38
Fe, mg/L	1.3	2.4	1.6	1.3
Mn, mg/L	0.2	0.5	0.2	0.2
Zn, mg/L	2	2	2	2
B, mg/kg	20	8	5	20

difference in efficiencies was due to the formation of insoluble sulfide. During the flotation, the H₂S underwent a stripping process, decreasing its concentration in the aqueous environment.

3.2 Soda ash production

The soda ash production process was performed following the flowchart depicted in Figure 2. PW and FPW streams were not used to produce soda ash due to the presence of dispersed oil, which was removed after surfactant and sodium carbonate treatment. In the production process, the two streams obtained after surfactant treatment (SPW and SFPW) and those generated after soda ash treatment (SCPW and SCFPW) were used. The initial streams evaporated until obtaining around 20% salt, and part of the obtained volumes were used to feed the batch reactor (Table 5). The slight differences in salt concentrations are explained by the fact that these waters were exposed to different treatments.

The amount of ammonium hydroxide solution added to the reactor, in each experiment, was calculated with an excess of approximately 10% with regard to the stoichiometry established in equations (4) and (5). This 10% excess margin was set to ensure bicarbonate anion formation. Bicarbonate anions are responsible for sodium bicarbonate precipitation.

The results of the physicochemical parameters for the streams rich in ammonium chloride are shown in Table 6. The sodium bicarbonate retained onto the filter after the reactor is shown in Table 7. Finally, the composition of the soda ash obtained after the thermal decomposition is shown in Table 8.

Metals like chromium, barium, nickel, copper, cadmium, silver, mercury, and lead were not detected in the samples. The absence of these metals indicates that they are not present as contaminant residue in these streams. The initial pH was around 7.5 and the final pH of all streams

Table 7. Composition of the precipitates obtained after the filtration stage.

Parameter	BSC	BS	BSF	BSCF
H ₂ O %	50	60	50	50
NaHCO ₃ %	27	23	15	23
Na ₂ CO ₃ %	-	-	-	-
(NH ₄) ₂ CO ₃	12	21	28	13.5
Free NH ₃ %	0	1.9	0	0
NaCl %	5.3	4.9	5.1	4.7
(Mg,Ca)CO ₃ %	<0.2	4	5	<0.2
K, mg/L	281	356	352	285
Fe, mg/kg	20	40	30	30
Mn, mg/kg	5	5	5	5
Zn, mg/kg	1.4	1.4	1.2	1.4
B, mg/kg	15	15	20	35
Ba, mg/kg	100	200	200	50

show values around 8.2. This increase can be due to the conversion of part of the ammonium chloride in hydroxide, increasing the pH.

The conductivity of the ammonium chloride streams increased when compared with the initial conductivity of the aqueous phase (see Table 4). This increase can be explained by the increase in the concentration of chloride anions after the evaporation stage. The average increase in the concentration of chloride anion was almost 200%.

The turbidity in the aqueous phases can be caused by two parameters, the presence of insoluble crystals and salt in the suspension alone, which were not retained onto the filter, or together with dispersed oil. In the case of the streams rich in ammonium chloride, the turbidity may be related to the first situation, namely, the sole presence of crystals and salt in the suspension.

Bicarbonate anions that are found in the streams rich in ammonium chloride (Table 6) derive from ammonium bicarbonate, which can be dissolved in an aqueous environment at concentrations as high as 78 g/L.

The experiment targeted a practically null concentration of carbonate anions in the final conditions of the reaction. Despite the predictions, the concentration of these anions in the streams showed values near 0.9g/L, as detailed in Table 6. It is important to highlight that such values are considered low when compared to the concentration of the bicarbonate anions, corresponding to 1%.

Ammonium was detected in streams rich in ammonium chloride, in both dissociated and non-dissociated forms, in a 10:1 ratio. Even though the ammonium represents a weak base with $pK_b = 1.78 \times 10^{-5}$, the presence of carbonate and bicarbonate anions shift their chemical balance to a concentration that causes an increase in the dissociated ammonium form.

The sodium concentration in streams rich in ammonium chloride, shown in Table 6, are lower than the initial average of 24% in treated PW and FPW (Table 4). This decrease is due to the sodium bicarbonate precipitation during the reaction. Calcium and Magnesium concentrations, shown in Table 6, when compared to those values in Table 4, show an increase in about 95% and indicate the precipitation of these metals in the bicarbonate form, along with sodium bicarbonate.

The presence of H₂S was not detected in the streams. The absence of H₂S indicates that, under high pH conditions, it could have reacted with a metal, producing a metal sulfide that precipitated, or it could have been desorbed with the carbon dioxide injected in the reactor. These hypotheses can be confirmed by the analysis of the produced soda ash, which shows the absence of H₂S. Table 7 breaks down the composition of the precipitates, which were produced in the reactor and obtained in the filtration stage.

After the reaction, H₂S, Cr, Ni, Cu, Cd, Ag, Hg, and Pb were not detected in the precipitate samples. The average humidity of the BSC, BS, BSF, and BSCF was around 50%. In these streams, the sodium bicarbonate levels reached an average

Table 8. Soda ash composition obtained after calcination.

Parameter	CSC	CS	CSF	CSCF	*Trona ore
Na ₂ CO ₃ %	83.6	72.1	59.8	83	69.7
NaCl %	16.4	15.4	20.3	17	ND
Mg ⁺² , Ca ⁺² %	<0.1	4.1	6.6	<0.1	1.72
Fe ⁺³ , mg/kg	62	125	120	108	1.503
Mn ⁺² , mg/kg	15	16	20	18	27.08
K ⁺ , g/kg	0.87	1.12	1.4	1.03	0.99
Zn ⁺² , mg/kg	4.3	4.4	4.8	5.1	6.13
B, mg/kg	47	47	80	126	23.14
Ba ⁺² , mg/kg	313	625	800	180	35.6

*Boerner et al. (1987)

value of 23%, and the sodium carbonate was not detected in any sample. These results were consistent with the purpose of this work, that was, to end the reaction with a pH of 7.5. Under this condition, the quantity of carbonate ions in relation to the bicarbonate is very low.

The ammonium carbonate was detected in these streams at an average concentration of 20%. For this type of process, this concentration is high, causing the decrease in the ammonium recovery efficiency in the process. A possible solution for this problem is to decrease the initial concentration of the ammonium hydroxide, which was added in excess in this experiment.

Sodium chloride was another non-desirable contaminant still existing in the sodium bicarbonate humid precipitate. The sodium chloride detected in the samples is the residue that did not react. At an average concentration level of 5%, sodium chloride can affect the quality of the produced soda ash, negatively impacting process efficiency.

Magnesium and calcium carbonates appeared in the surfactant-treated streams, but were not detected in the soda ash treated ones. This indicates that the treatment with soda ash is more efficient in the removal of these metals. Table 8 shows the soda ash compositions obtained in this work, as well as the chemical compositions of trona ore - Na₃(CO₃)(HCO₃).2H₂O (Boerner et al., 1987).

Examining the data, one can imply that the higher the level of sodium chloride is, the lower the level of the sodium carbonate will be. This relates to the efficiency of the process, which can be improved by adjusting the reactant concentrations.

The concentrations of calcium and magnesium in the soda ash samples show that the treatment of PW and FPW with soda ash decreased the levels of these materials to values lower than 0.1%. The samples treated with surfactant show values up to 6%, which are very high, even when compared to the trona ore ones. The surfactant efficiency in the treatment of produced water can be improved by using higher concentrations of it.

The metals iron and manganese showed lower concentrations than the ones of the trona ore. This did not happen with barium. When comparing the presence of barium in the soda ash in contrast with the trona ore results, the first one presented a higher ratio.

Similarly to the bicarbonate stream results, the values of H₂S, Cr, Ni, Cu, Cd, Ag, Hg, and Pb were not detected in the soda ash streams. Boron, potassium, and zinc concentrations were similar to the trona ones. This indicates that these metals would not pose a severe contamination problem. The same treatment effected with the trona ore to obtain soda ash could be reproduced in the present work.

4. CONCLUSIONS

This paper raised the possibility of producing sodium carbonate using produced water. The main findings from this research are summarized as follows:

1. The sodium carbonate yields were as high as 80%. Changes in operational conditions still can show improvements;

2. The purity of the obtained sodium carbonate depends especially on the presence of calcium and magnesium, which can be minimized by performing a previous treatment step with soda ash or surfactant, however at higher concentrations than those used in the present work;

3. Other metals that can decrease the quality of the obtained soda ash were found at different concentrations, but those that showed the highest ratios in comparison to the trona ore are prone to be treated;

4. The surfactant treatment promoted a clearance of about 100% of the dispersed oil. This treatment was important to eliminate the oil presence in the soda ash;

5. This process is innovative in the produced water treatment field, because it transforms an effluent that is harmful to the environment into a raw material capable of producing soda ash.

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