

## A study of the factors that contribute to the corrosion process in produced water samples: a multivariate analysis approach

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### ABSTRACT

Due to the exploration and production of oil in new oil fields, significant volumes of produced water are being extracted. In maritime platforms, seawater is used as injection water, due to its availability. However, the mixing of seawater and formation water might create fouling. In this study, quantitative investigations into the relationships among 14 chemical properties in different oil fields were carried out. With the aim to correlate the variables measured in produced water samples and the corrosive process regarding them. For this, the multivariate analysis statistical methods principal component analysis (PCA) and hierarchical clustering on principal components (HCPC) were used. The results show that chemical properties such as sulfate are inversely correlated to formate, bicarbonate, and acetate. Furthermore, the PCA results indicated that, the most influential chemical properties in the produced water samples were chloride, bromide, sulfate, calcium, and strontium. However, it was not possible to visualize the division of clusters. Only, the separation of clusters was observed, in the combination of PCA with HCPC. Where the different dominant factors in the characteristic of interest were showed. The samples, therefore, are classified into three clusters, namely: cluster 1, cluster 2, and cluster 3, for the purpose of discussion.

*Keywords:* Produced water; Fouling; Multivariate analysis; Injection water; Scaling

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## 1. Introduction

Due to the exploration and production of new oil fields, as offshore oil platforms located in deep waters, oil production activities have intensified, and significant volumes of produced water are being extracted. At the beginning of production, oil fields generate small quantities of produced water, but this production increases with time, reaching values in the final stage of production [1–3]. The composition of the produced water depends on the age and geology of the rock formations and the recovery processes; it can contain a complex mixture of organic and inorganic compounds, toxic elements, radioactive materials, and chemicals added during the petroleum production process [4]. Therefore, produced water presents higher concentrations of dissolved salts compared to seawater [5]. The water naturally present in the geological formation of an oil reservoir is in chemical equilibrium with the environment. However, by injecting water into the reservoir to increase production, a disturbance of the natural state of the system can occur, causing the precipitation of salts in the walls of the pipes' walls [6–8]. The intensity of the occurrence of precipitation is related to the cationic and anionic composition of the produced water [9].

Because maritime oil platforms use seawater as injection water due to its greater availability [7,10–14], high concentrations of ions, such as sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), ( $\text{Ca}^{2+}$ ), barium ( $\text{Ba}^{2+}$ ) and strontium ( $\text{Sr}^{2+}$ ), can cause precipitation based on the formation of  $\text{CaSO}_4$ ,  $\text{BaSO}_4$  and  $\text{SrSO}_4$  [7,13–17]. In addition,  $\text{CO}_2$  can precipitate in the form of  $\text{CaCO}_3$ , which is naturally present in formation water [1,16,18]. Because scaling is common in many regions of the world, and the removal of saline deposits has a great impact on the cost of production, knowledge of its mechanism of formation, the type and amount of deposition, and its location are essential for preventive and/or corrective measures [14,16,19,20]. With the purpose of knowing the composition of the mixture of waters associated with petroleum to prevent the formation of saline deposits, which adhere in oil-conducting pipes, and can cause stops in the process, it is important to monitor each oil reservoir [6,15,16,21].

Monitoring the produced waters in oil fields plays an important role in the exploration and production of oil, because the problems associated with corrosion in secondary recovery operation of the injection water systems could be avoided, the amount of some ions could be controlled to avoid their reaction with other ions, and their compatibility with other types of injection water could be evaluated [22,23].

The oil fields analyzed in this work are in the Mundaú sub-basin, Ceará Basin, about 95 km northwest of the city of Fortaleza, capital of the state of Ceará (Fig. 1). Located on the Brazilian Equatorial Margin. The Ceará Basin is limited to the southeast with the Potiguar Basin, through Alto de Fortaleza; to the west with the Barreirinhas Basin, through Alto de Tutóia; to the south, by the outcrop of the basement; and to the north, by the Ceará Transformer Fault, associated with the Romanche Fracture Zone [24]. A sub-basin of Mundaú, Bacia do Ceará, is a region that produces oil and gas with four producing fields in its shallow waters. It is located approximately 30 km from the coast

and has 32 reservoirs in production and 9 fixed platforms. This basin is classified as a new frontier basin, as the portion of deep water is still little known and unexplored. The first deepwater discovery occurred recently in 2012 [25].

This paper intends to focus on the composition of the water mixture associated with oil in a multivariate statistical approach. With the objective of identifying the variables that contribute to the corrosion process in produced water samples in the state of Ceará – Brazil, using the concentrations of the ion as input variables in the statistical methods of principal component analysis (PCA) and the hierarchical clustering on principal components (HCPC).

## 2. Materials and methods

### 2.1. Reagents and materials

All reagents used were of analytical grade, and the water (resistivity of 18.2 M $\Omega$  cm) was purified in a Milli-Q system (Millipore, Bedford, MA, USA).

Stock aqueous solutions of cations (1,000 mg/L) were purchased from Ultra Scientific (USA). The analytical calibration curve was prepared in concentrations of 1.0, 10.0, 20.0 and 30 mg/L in 1%  $\text{HNO}_3$  for the cations of sodium, potassium, calcium, and magnesium. For the stock aqueous solutions of barium, iron, lithium and strontium, calibration curves were prepared in concentrations of 0.5, 1.0, 5.0 and 10.0 mg/L in 1%  $\text{HNO}_3$ .

In relation to the anions, a stock solution of inorganic anion multielement (400 mg/L) was purchased from DIONEX (USA), and a stock solution of organic acids multielement (1,000 mg/L) was purchased from SPECSOL (QUIMLAB, SP, Brazil).

### 2.2. Sampling

Samples of produced water were collected in the production fields located in the Mundaú sub-basin in the Ceará State Basin, totaling 230 samples from 37 oil wells localized in four oil fields. Table 1 shows the distribution of the number of production wells per production field.

The sampling plan and collection were carried out by the oil and gas company. To ensure and preserve the characteristics of the samples, from collection to the moment of their analysis, conservation procedures were used. These procedures take into account the preservative agent, the type of container and the appropriate volume for determining each parameter. After collection, the material preserved in ice was sent to the laboratory to carry out the analyzes requested by the aforementioned company.

### 2.3. Chemical analysis

#### 2.3.1. Instrumentation and procedures

The cations ( $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and total Fe) and anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCO}_3^-$  and  $\text{HCOO}^-$ ) were quantified from the collected samples.

Cation analysis was performed by simultaneous inductively coupled plasma optical emission spectrometer with axial and radial views (Optima 4300 series, Perkin Elmer, USA). The plasma gas argon flow was 15 L/min, the



Fig. 1. Location of the sub-basin of Mundaú, Bacia do Ceará, a new deep water exploration frontier in the Brazilian Equatorial Margin.

Table 1  
Amount of oil wells per production oil field

Oil fields	Oil wells	Development area	Latitude/Longitude	Deep water
A	A00, A04, A07, A11, A12, A14, A18, A21, A22	44.00 km <sup>2</sup>	2°58'41.1"S 38°57'38.7"W	44 m
B	B02, B04, B07, B11, B14, B13, B17, B22, B24	21.34 km <sup>2</sup>	3°05'26.8"S 38°46'45.6"W	46 m
C	C37, C84, C86	22.67 km <sup>2</sup>	3°07'59.1"S 38°49'19.9"W	36 m
D	D00, D01, D03, D08, D09, D11, D12, D13, D14, D15, D17, D19, D25, D28, D36, D38	20.00 km <sup>2</sup>	3°01'50.4"S 39°02'43.3"W	32 m

"LETTER" – production field; "NUMBER" – oil well production.  
Source: ANP (2019).

auxiliary argon gas flow was 0.5 L/min, and the flow of argon gas from the nebulizer was 0.8 L/min. A nebulizer system, nebulizer chamber, crossflow type, and Scott-Fassel type were used. The frequency generator and radio-frequency power were 40 MHz and 1.1 kW, respectively.

Anion analysis was performed using an ion chromatograph (ICS-3000, Dionex Corporation, USA). The chromatographic column was an AS18 column (4 × 250 mm), with a Suppressor ASRS® Ultra II, 4 mm. Other components

included a conductivity detector, a 25 µL loop, an AG 18 guard column (4 mm × 50 mm), and a potassium hydroxide (KOH) eluent generator. The elution program used the following steps: the concentration was 10.0 mmol between 0 and 10 min, it increased to 22 mmol by 13.2 min, it increased further to 44 mmol by 13.44 min, and it was maintained at 44 mmol until 15.0 min. The column temperature was 30°C. The current was 40 mA, the elution flow was 1 mL/min, and the conductivity was 0.6 µS.

Bicarbonate ion analysis was performed using an automatic potentiometric titrator with a piston burette, a volume of 20 mL, and a precision of 0.01 mL (809 Titrando, Metrohm) for the addition of the titrant solution (HCL, concentration 0.1 mol/L). The potentiometric titration assays followed the procedure described by Standard Methods (APHA 2320B). The equipment was calibrated with the pH 4.0 and 7.0 solutions, prior to use.

The analytical calibration curves of bromide, chloride and sulfate anions were prepared at concentrations of 0.04, 2.0, 4.0, 20.0 and 40.0 mg/L. For organic acids, the analytical calibration curves were prepared at the concentrations of 0.5, 1.0, 5.0 and 10.0 mg/L using a multielement stock solution of acetate and formate.

#### 2.4. Multivariate statistical analysis

In multivariate statistics, the PCA is a useful tool that can be applied to visualize the data structure, find similarities between samples, and detect anomalous samples (outliers) [26–28]. Meanwhile HCPC represents a set of exploratory techniques, which can be applied when there is an intention to verify the existence of similar behavior among certain variables, with the objective creates clusters, in which internal homogeneity prevails. For this, it is used as a pre-processing step for data sets in the tool PCA, before performing the grouping methods, in order to reduce data noise [29,30].

Therefore, these two multivariate statistical techniques were combined in conducting the analysis to describe and visualize the similarity between the variables. The techniques were applied to water samples produced with the package FactoMineR [30], available in language R [31]. In the PCA, variables were reduced using objective criteria, allowing the construction of two-dimensional or three-dimensional graphs. This facilitates the observing of data in a few dimensions, preserving the greatest amount of information possible. For this, the dimensionality of the original data set was reduced to a new system of axes, called main components (CP). Where matrix  $X$  is decomposed into a product of two matrices called scores and loadings. The scores represent the similarity relationships between the samples, since the evaluation of the loadings (weights) allows us to understand which variables most contribute to the groupings shown in the score graph. The number of main components to be used is determined by the percentage of explained variance. Thus, several components are selected in such a way that the largest percentage of the variation present in the original data set is retained. After the selection of the main components, the HCPC was performed based on the Euclidean distance measurement and Ward's method, as it sought to generate clusters that have a high internal homogeneity [32,33].

To measure the adequacy of samples of the produced water, the Kaiser-Meyer-Olkin test (KMO) was performed. The KMO values show the proportion of variance that the parameters have in common, with KMO values between 0.6 and 0.7 being reasonable; already considered average KMO values between 0.7 and 0.8, and considered adequate KMO values between 0.8 and 1. The communalities indicate the proportion of variance for each variable

included in the analysis is explained by the extracted components, in which usually, the minimum value of 0.50 is accepted for the extraction of the main components, it was used to the Kaiser standard, where only if the components whose eigenvalues are higher than 1, were extracted [34].

### 3. Results and discussion

Samples were collected from 37 wells in four different oil fields. In this study, just the parameters that generated values above detection limits in all samples were considered. Chemical analyses can be classified into two groups: anions and cations. Quantitative analysis of each sample was conducted for three replicates. The contents are expressed as means and standard deviation. The calculated main contents were then subjected to multivariable statistical analysis.

#### 3.1. Elemental concentration

Tables 2 and 3 show the statistical summary for the concentrations of variables: cations and anions, in the produced water samples of the oil fields studied that were collected from 2009 to 2012.

The mean concentrations of sulfate are generally low, barium and other elements that could form insoluble sulfates may be present in solution in high concentrations. However, the mean concentrations of field B presented high concentrations of sulfate; similar results were also found in another study [35]. In this case, barium and calcium may precipitate as incrustation in the production tubes according to other authors [16,36].

In general, their mean concentrations follow the order  $\text{Cl}^- > \text{Na}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Sr}^{2+}$ ,  $\text{Br}^-$ , Total Fe,  $\text{Ba}^{2+}$ ,  $\text{HCOO}^-$  and  $\text{Li}^+$ . These results are like to previous reports [22,37,38].

Among the producing fields studied, field D presented the highest amount of acetate in its produced water samples. These results probably occur due to a decrease in the content of saturated hydrocarbons and consequently in the API's (American Petroleum Institute) grade of the oil. In quantitative increase, both in density, in viscosity, and in oil composition. Consequently, a reduction in production took place, as such as, refining efficiency, and an increase in the process costs [39].

Since petroleum can suffer changes in its composition due to biodegradation during the migration process, biodegradation is a process of altering crude oil by different microorganisms. At the end of this process, hydrocarbons are transformed into metabolites, such as organic acids, acetate and formate, and/or carbon dioxide [39,40].

#### 3.2. Principal component analysis

Fig. 2 shows the representation of individuals (samples) and variables (cations and anions) in the factorial plane resulting in the first and second main components. It can be observed that, in the PCA algorithm, the first three principal components explain approximately 73.15% of the accumulated variance of the data set, before distribution in 14 dimensions. In other words, the data set before

Table 2  
Concentrations of cations in produced water of production fields in the Ceará State Basin (2009–2012)

Sampling sites	(mg/L)	Ba <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Total Fe	Li <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>
Field A	Average	210.1	6,248.7	427.4	49.3	5.6	934.0	930.4	26,150.3
	Max.	402.9	9,468	644.2	107.4	12.5	1,217.4	2,366	34,625.0
	Min.	2.03	3,180	150.1	5.3	0.01	505.5	445.9	15,255.0
Field B	Average	63.3	2,846.6	186.6	18.2	4.2	947.6	430.8	16,340.2
	Max.	237.3	7,685.5	560.9	79.7	16.1	1817.0	730.1	27,645.0
	Min.	<LOD	511.1	21.1	0.01	0.01	636.5	240.5	9,163.5
Field C	Average	50.4	3,385.4	230.4	20.3	4.0	743.8	375.3	22,518.3
	Max.	128.2	4,781	372.9	42.1	16.8	1,230.5	626.1	29,760.0
	Min.	1.6	1,352.4	116.2	2.1	0.01	279.0	93.7	16,610.0
Field D	Average	18.9	3,700.1	229.4	31.5	3.6	1,034.2	380.2	22,603.8
	Max.	86.4	5,868.5	440.5	120.1	14.3	1,889.5	700.5	32,940.0
	Min.	<LOD	659.7	0.05	<LOD	<LOD	642	135.1	10,875.0

LOD = limit of detection.

Table 3  
Concentrations of anions in produced water of production fields in the Ceará State Basin (2009–2012)

Sampling sites	(mg/L)	CH <sub>3</sub> COO <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>	HCOO <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Field A	Average	303.1	511.0	313.0	53,920.7	11.5	252.2
	Max.	786.8	835.6	508.1	65,001.1	47.1	2,135.8
	Min.	<LOD	104.3	112.5	30,123.9	<LOD	<LOD
Field B	Average	174.3	481.6	147.6	32,468.1	9.3	1,563.8
	Max.	625.7	708.5	384.4	55,876.2	74.1	4,010.5
	Min.	<LOD	307.1	41.9	20,004.4	<LOD	<LOD
Field C	Average	280.0	483.1	277.9	42,117.2	14.6	315.3
	Max.	458.8	709.1	815.3	45,319.2	35.5	686.5
	Min.	51.1	346.7	189.2	39,335.3	<LOD	<LOD
Field D	Average	545.7	793.4	225.1	43,600.6	20.4	440.3
	Max.	1541.0	1,910.3	367.7	55,640.1	106	3,161.1
	Min.	<LOD	133.3	56.4	20,506.4	<LOD	<LOD

LOD = limit of detection.

distribution was explained by fourteen dimensions, but then, only three dimensions are required to explain the variation in the data set. This denotes that the originals variables are correlated with each other, and so the first components explain a good portion of the variance of the data.

The representation of variables shows the distribution of the values of the weights for the produced water samples in relation to the first main component (CP1) vs. the second main component (CP2). For analysis, the weights of the variables in the main components were values larger than 0.7 in the module. The variable weights describe the influence of each original variable in the construction of each major component. The first main component describes the chloride (Cl), with a weight of 0.94, followed by bromide (Br), with a weight of 0.82, sulfate (Sulf), with a weight of 0.85, calcium (Ca), with a weight of 0.91, and strontium (Sr), with a weight of 0.91. The variables formate (For), with a weight of 0.84, bicarbonate (Bc), with a weight of 0.82 and acetate (Act), with a weight of 0.77, are related in importance

with the second main component. The third main component describes the variation of the magnesium (Mg), with a weight of 0.88, as shown in Table 4.

The KMO value was equal to 0.85, considered adequate for the sample set. Then, main components were chosen with eigenvalues greater than 1. For each main component, the variables with the highest score were evaluated: Act 0.74, Bc 0.79, Ba 0.84, Br 0.95, Ca 0.82, CL 0.85, Sr 0.87, FeT 0.81, For 0.76, Li 0.90, Mg 0.34, K 0.84, Na 0.92 and Sulf 0.93.

In relation to the representation of variables in the factorial plan, the vectors that are more distant from zero correspond to the variables of greater influence on the value of the main component, while the vectors that are closer to zero indicate variables with little influence on the main component, as shown in Fig. 2b [41]. As indicated below (Fig. 2b), the variables acetate, bicarbonate, and formate are positively correlated with each other, which means that samples of water produced with a high concentration of acetate, tend to have a high concentration of bicarbonate

Table 4  
PCA loadings of cation and anions on significant for the first three principal component

Variables	PC1	PC2	PC3
Acetate	0.48	<b>0.77</b>	0.24
Bicarbonate	0.41	<b>0.82</b>	0.10
Bromide	<b>0.83</b>	-0.08	-0.05
Strontium	<b>0.91</b>	-0.29	-0.03
Chloride	<b>0.95</b>	0.01	-0.07
Calcium	<b>0.91</b>	-0.15	-0.15
Formate	0.16	<b>0.84</b>	-0.20
Magnesium	0.10	-0.15	<b>0.89</b>
Sodium	<b>0.88</b>	0.09	0.18
Sulfate	<b>-0.85</b>	-0.23	0.03
Eigen values	<b>6.23</b>	<b>2.67</b>	<b>1.34</b>
Variance	<b>44.51</b>	<b>19.06</b>	<b>9.58</b>
Cumulative variance	<b>44.51</b>	<b>63.57</b>	<b>73.15</b>

Bold values represent the main loadings of principal component.

and formate. And that the variables formate (For), bicarbonate (Bc) and acetate (Act) are inversely correlated with the sulfate variable (Sulf). This leads us to conclude that in the samples studied, high concentrations of the formate (For), bicarbonate (Bc) and acetate (Act) variables trend to correspond to low concentrations of the sulfate variable (Sulf) or the other way around.

Regarding the analysis of the individuals (Fig. 2a), the oil wells have remarkably similar profiles, with relatively close concentration values for all variables. The samples presented homogeneity in the selected characteristics. Therefore, it was not possible to visualize the division of clusters, but the predominance of certain characteristics

in the samples was verified, except for some producing wells in field A and field D, which are very distinct regions, regarding each other, indicating that the chemical compositions of these producing wells have different characteristics.

### 3.3. Hierarchical clustering on principal components

By using the classification of the HCPC from the information of the first three components of the PCA, it was possible to identify three clusters. For each cluster, the contributions of the most important components and variables were highlighted. Fig. 3 shows the presence of three large clusters of samples, differentiated by three different colors: blue, yellow, and grey. These three clusters occupy vastly different regions, and therefore, the differences in the chemical compositions of each cluster can be deduced.

#### 3.3.1. Chemical profile of cluster

*Cluster 1 (blue)* – related to the following oil wells: A12, B02, B04, B07, B11, B13, B14, C37, D01, D03, D09, D11, D25, D28. The produced water samples from these oil wells feature intermediate concentrations of calcium, chloride, bromide, strontium, and sodium and high concentrations of sulfate. In this cluster, as seen by the main features, there is a propensity to form fouling salts, as indicated by the high concentrations of sulfate anions and the intermediate concentrations of cations, calcium, and strontium, as seen in Table 5. Because sulfate control is important for the petroleum industry, the supersaturation of this anion associated with the cations calcium, barium, and strontium results in the formation of sulfate precipitates. These precipitates are adherent, almost insoluble in mineral acids or other common solvents, and difficult to remove mechanically; further, they can cause severe flow restrictions within the drainage radius inside a formation, of a well, and in other

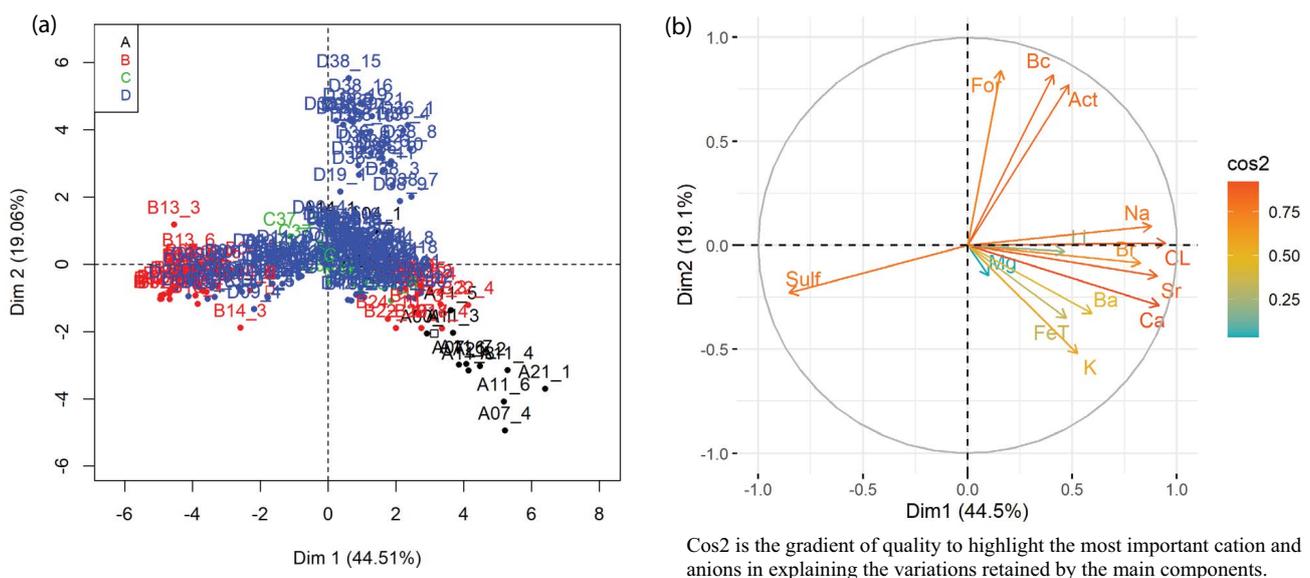


Fig. 2. Representation of samples and variables in the factorial plan: (a) samples in the factor map (PCA). Where “LETTER” – production field; “NUMBER\_NUMBER” – sampling at different periods of collection of the corresponding oil wells. (b) Cation and anions in the factor map (PCA).

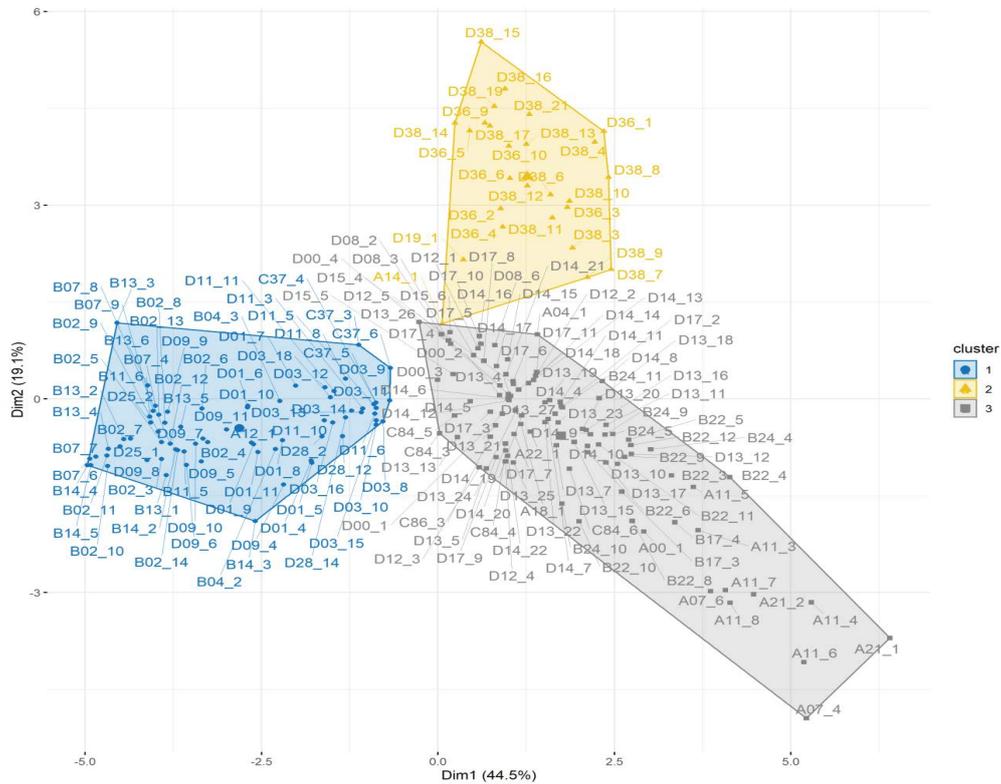


Fig. 3. Representation of samples illustrating the clusters (HCPC), in the factorial plan. Where “LETTER” – production field; “NUMBER\_NUMBER” – sampling at different periods of collection of the corresponding oil wells.

Table 5  
Classification of clusters from oil well identified by the most important variables in the PCA

Cluster	Main variables	Oil wells
1 – blue	Sulfate (Sulf)	A12, B02, B07, B04, B11, B13, B14, C37, D01, D03, D09, D11, D25, D28
2 – yellow	Formate (For), bicarbonate (Bc) and acetate (Act)	A14, D19, D36, D38
3 – grey	Bromide (Br), chloride (Cl), calcium (Ca), strontium (Sr), sodium (Na)	A00, A04, A07, A11, A18, A21, A22, B17, B22, B24, C84, C86, D00, D08, D12, D13, D14, D15, D17

“LETTER” – production field; “NUMBER” – oil well production.

equipment and during processing [15,16,35]. However, it is important to emphasize that it is common practice to use seawater in injection operations due to its availability, regardless of the high concentrations of sulfate, and to try later to remedy the problems generated [7,11,35]. Another problem associated with the high concentrations of sulfate in produced water is the reduction of sulfate to sulfide by the activity of microorganisms, which encourages corrosion during oil and gas processing. Moreover, it reduces the quality of fossil fuels by souring (i.e., the intense generation of sulfuric gas) of the reserve [35].

Cluster 2 (yellow) – related to the following oil wells: A14, D19, D36, D38, as seen in Table 5. The oil wells of this group occupy distinct regions that are under the influence of the variables bicarbonate, formate and acetate, which are inversely correlated with the sulfate variable (Sulf).

The samples grouped in cluster 2 might show a tendency for the deposition of insoluble compounds, due to large amounts of sodium bicarbonate that can generate incrustations from the precipitation of the salt as carbonates, according to general equation [Eq. (1)]. These incrustations tend to deposit on the walls of pipes and grow over time, causing inconveniences such as a reduction in pipe sections, fractures in the film, a reduction in pressure, a decrease in oil flow, and a consequent increase in energy consumption [21,40].



Cluster 3 (grey) – related to the following oil wells: A00, A04, A07, A11, A18, A21, A22, B17, B22, B24, C84, C86, D00,

D08, D12, D13, D14, D15, D17. These oil wells occupy regions near each other and show an overlap, which indicates similarity in their chemical compositions. Given the composition of these fields, as shown in Table 5, high concentrations of calcium, chloride, bromide, sodium, and strontium might imply lower sulfate concentrations, since they are inversely correlated according to Fig. 2b.

The main characteristics predominant in the samples of produced water in the second cluster can generate a propensity for corrosion, as evidenced by the high concentrations of chloride and sodium variables. It is noteworthy that the influence of this anion on corrosion is through the destruction of the passivation of stainless steels and aluminum alloys. As a strong electrolyte, it causes an increase in conductivity [42,43]. Moreover, iron is corroded more rapidly in dilute solutions of NaCl (dissolved salts effect) because the dissolved oxygen can reach the cathodic areas (depolarizing action) and consume the electrons generated in the anodic reaction, implying an increase of the corrosion speed [44,45].

In Fig. 4, the individuals are classified for generating clusters in different hierarchical levels represented by a dendrogram, in which the produced waters studied were grouped based on the similarity of the characteristics selected as the most important in the PCA and using the Euclidean distance. It was observed that the optimal cut-off point for the formation of similarity clusters was approximately 30%; thus, a greater distancing occurs in the measure of similarity for the formation of the clusters. The clusters were formed by the similarity between the concentrations of the quality characteristics evaluated, and it can be observed that the characteristics related to salinity were the ones that most influenced the separation of the clusters.

It is verified that cluster I is significantly different from the other cluster by the sulfate parameter. In cluster 3, it

was observed that the most influential characteristics for the formation of the cluster were bromide, calcium, chloride, sulfate, sodium, and strontium ions. Cluster 2 is significantly different from the other cluster by the parameter's acetate, bicarbonate and formate.

Finally, the result obtained from the PCA indicates that it was not possible to visualize the division of the clusters, but the predominance of certain characteristics was verified. Meantime, the combination of PCA with HCPC showed the different dominant factors in the characteristic of interest. The separation of three groups due to the predominant characteristics in each group was observed. In which were identified by three different colors: blue, yellow, and grey. These three groups occupy very different regions and, therefore, the differences in the chemical compositions of each group can be deduced. Both tools have been used previously in the analysis of environmental data in other studies [26,27,46]. As expected, in this study, both tools complemented each other, for it allows us to correlate the measured variables with the corrosive process.

#### 4. Conclusions

In this work, quantitative investigations into the relationships among 14 chemical properties and samples in different oil wells and oil fields were carried out. The PCA and HCPC exploratory techniques together helped in interpreting the data sets. In the PCA analysis, it was not possible to visualize the division of clusters, but the predominance of certain characteristics in the samples of produced water were verified. In the HCPC, it was possible to divide three clusters based in the information of the first three components of the PCA. The main characteristic in the produced water samples was the formation of fouling salts, as evidenced by the high concentrations of the sulfate anion and the intermediate concentrations of the cations calcium and strontium in cluster 1. In the samples of produced water in cluster 2, a tendency toward the deposition of insoluble compounds was observed due to the high concentration of bicarbonate anion. In the produced water samples in cluster 3, due to the high concentrations of the chloride and sodium variables, a propensity to corrosion was indicated.

In relation to the predominant characteristics for each cluster, it can be said that cluster 3 presents a tendency to corrosion, as evidenced by the high concentration of chloride. It is noteworthy that the influence of this anion on corrosion is through the destruction of the passivation of stainless steels and aluminum alloys. To avoid fouling due to the deposition of insoluble and insoluble salts in clusters 1 and 2, it is necessary to control the sulfate anion because the supersaturation of this anion, which is associated with the cations calcium, barium and strontium, results in the formation of sulfate precipitates ( $\text{CaSO}_4$ ,  $\text{BaSO}_4$  and/or  $\text{SrSO}_4$ ) and the control of the bicarbonate anion, which can generate fouling from the precipitation of the salts as carbonates. This can result in operational problems, such as the loss of fluid pressure due to a reduction in the diameter of pipes, a decrease in production flow and a consequent increase in energy consumption. Further, it can lead to additional capital costs and substantial operational costs.

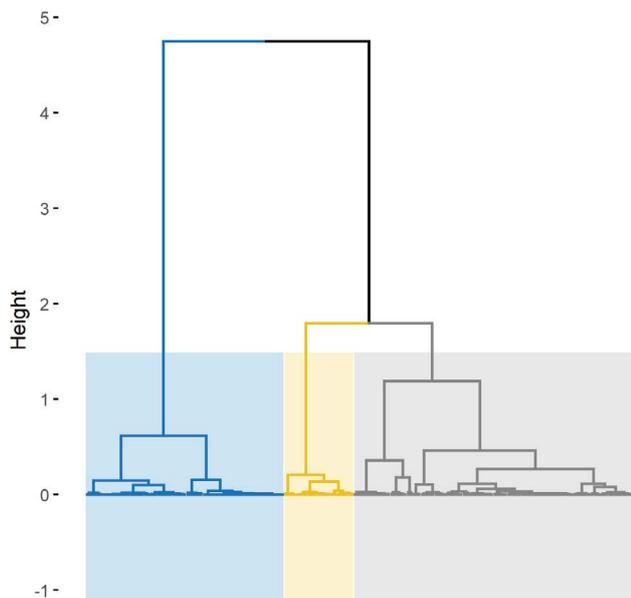


Fig. 4. Dendrogram obtained by hierarchical clustering analysis of cations e anions. Where the clusters are represented for colors: blue – cluster 1; yellow – cluster 2; grey – cluster 3.

This study allowed to correlate the variables measured in produced water samples from the oil production process in the state of Ceará, and thus, to aid in understanding the interrelationship of the variables, in a synergy between the corrosive process and the statistical tools.

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### References

- [1] D. Dudášová, G. Rune Flåten, J. Sjöblom, G. Øye, Stability of binary and ternary model oil-field particle suspensions: a multivariate analysis approach, *J. Colloid Interface Sci.*, 337 (2009) 464–471.
- [2] K.S.L. Figueredo, C.A. Martínez-Huitile, A.B.R. Teixeira, A.L.S. de Pinho, C.A. Vivacqua, D.R. Silva, Study of produced water using hydrochemistry and multivariate statistics in different production zones of mature fields in the Potiguar Basin – Brazil, *J. Pet. Sci. Eng.*, 116 (2014) 109–114.
- [3] P.H.M. Vasconcelos, A.L.M. Camelo, A.C.A. de Lima, H.O. do Nascimento, C.B. Vidal, R.F. do Nascimento, G.S. Lopes, E. Longhinotti, Chemometric tools applied to optimize a fast solid-phase microextraction method for analysis of polycyclic aromatic hydrocarbons in produced water, *Environ. Sci. Pollut. Res.*, 28 (2021) 8012–8021.
- [4] K. AlAnezi, M. Belkharouch, S. Alali, W. Abuhaimed, Produced water characterization in Kuwait and its impact on environment, *Desal. Water Treat.*, 51 (2013) 302–306.
- [5] A.G. Collins, *Developments in Petroleum Science 1*, in: *Geochemistry Oilf. Waters*, Elsevier Sci., Amsterdam, 1975.
- [6] S. Hajrezaie, X. Wu, C.A. Peters, Scale formation in porous media and its impact on reservoir performance during water flooding, *J. Nat. Gas Sci. Eng.*, 39 (2017) 188–202.
- [7] P.G. Bedrikovetsky, E.J. Mackay, R.M.P. Silva, F.M.R. Patricio, F.F. Rosário, Produced water re-injection with seawater treated by sulphate reduction plant: injectivity decline, analytical model, *J. Pet. Sci. Eng.*, 68 (2009) 19–28.
- [8] S. Naseri, J. Moghadasi, M. Jamialahmadi, Effect of temperature and calcium ion concentration on permeability reduction due to composite barium and calcium sulfate precipitation in porous media, *J. Nat. Gas Sci. Eng.*, 22 (2015) 299–312.
- [9] F.R. Cavalcante, G.D.C. Santana, E.D.M. Chaves, K.A. Kodel, Desenvolvimento de dispositivo eletromagnético para prevenção do processo de incrustação em dutos de petróleo, *Rev. Geintec - Gestão, Inovação e Tecnol.*, 2 (2012) 1–11.
- [10] M.S.H. Bader, Sulfate scale problems in oil fields water injection operations, *Desalination*, 201 (2006) 100–105.
- [11] H.J. Bayona, A Review of Well Injectivity Performance in Saudi Arabia’s Ghawar Field Seawater Injection Program, Middle East Oil Show, Bahrain, 1993.
- [12] M. Salman, H. Qabazard, M. Moshfeghian, Water scaling case studies in a Kuwaiti oil field, *J. Pet. Sci. Eng.*, 55 (2007) 48–55.
- [13] A.B. Bin Merdhan, A.A.M. Yassin, Scale formation in oil reservoir during water injection at high-salinity formation water, *J. Appl. Sci.*, 7 (2007) 3198–3207.
- [14] A.B. Bin Merdhan, A.A.M. Yassin, M.A. Muherei, Laboratory and prediction of barium sulfate scaling at high-barium formation water, *J. Pet. Sci. Eng.*, 70 (2010) 79–88.
- [15] J. Moghadasi, M. Jamialahmadi, H. Müller-Steinhagen, A. Sharif, Formation Damage Due to Scale Formation in Porous Media Resulting From Water Injection, SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisiana, 2004.
- [16] M. El-Said, M. Ramzi, T. Abdel-Moghny, Analysis of oilfield waters by ion chromatography to determine the composition of scale deposition, *Desalination*, 249 (2009) 748–756.
- [17] Y. Liu, A. Kan, Z. Zhang, C. Yan, F. Yan, F. Zhang, N. Bhandari, Z. Dai, G. Ruan, L. Wang, J. Greenberg, M. Tomson, An assay method to determine mineral scale inhibitor efficiency in produced water, *J. Pet. Sci. Eng.*, 143 (2016) 103–112.
- [18] M. Stewart, K. Arnold, Part 1 – Produced Water Treating Systems, *Produced Water Treatment Field Manual*, Elsevier, Boston, 2011, 1–134.
- [19] M. Crabtree, D. Eslinger, P. Fletcher, M. Miller, A. Johnson, G. King, La lucha contra las incrustaciones—Remoción y prevención, *Oilfield Review*, 2009.
- [20] A.A. Olajire, A review of oilfield scale management technology for oil and gas production, *J. Pet. Sci. Eng.*, 135 (2015) 723–737.
- [21] M. Kamalipour, S.A.M. Dehghani, A. Naseri, S. Abbasi, Role of agitation and temperature on calcium sulfate crystallization in water injection process, *J. Pet. Sci. Eng.*, 151 (2017) 362–372.
- [22] G. Jing, S. Tang, X. Li, H. Wang, The analysis of scaling mechanism for water-injection pipe columns in the Daqing Oilfield, *Arabian J. Chem.*, 10 (2017) S1235–S1239.
- [23] W. Naessens, T. Maere, G. Gilabert-Oriol, V. Garcia-Molina, I. Nopens, PCA as tool for intelligent ultrafiltration for reverse osmosis seawater desalination pretreatment, *Desalination*, 419 (2017) 188–196.
- [24] K.M.L. Oliveira, H. Bedle, R.M.G.C. Branco, A.C.B. de Souza, F.N. Filho, M.N. Normando, N.M. de Almeida, T.H.S. Barbosa, Seismic stratigraphic patterns and characterization of deepwater reservoirs of the Mundaú sub-basin, Brazilian Equatorial Margin, *Mar. Pet. Geol.*, 116 (2020) 104310, <https://doi.org/10.1016/j.marpetgeo.2020.104310>.
- [25] N.M. de Almeida, T.M. Alves, F.N. Nepomuceno Filho, G.S.S. Freire, A.C.B. de Souza, M.N. Normando, K.M.L. Oliveira, T.H.S. Barbosa, Tectono-sedimentary evolution and petroleum systems of the Mundaú subbasin: a new deep-water exploration frontier in equatorial Brazil, *Am. Assoc. Pet. Geol. Bull.*, 104 (2020) 795–824.
- [26] A. Chandrasekaran, R. Ravisankar, N. Harikrishnan, K.K. Satapathy, M.V.R. Prasad, K.V. Kanagasabapathy, Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India – spectroscopical approach, *Spectrochim. Acta, Part A*, 137 (2015) 589–600.
- [27] S. Parra, M.A. Bravo, W. Quiroz, T. Moreno, A. Karanasiou, O. Font, V. Vidal, F. Cereceda-Balic, Source apportionment for contaminated soils using multivariate statistical methods, *Chemom. Intell. Lab. Syst.*, 138 (2014) 127–132.
- [28] E. Karpushkin, A. Bogomolov, Morphology assessment of poly(2-hydroxyethyl methacrylate) hydrogels using multivariate analysis of viscoelastic and swelling properties, *Polymer (Guildf)*, 58 (2015) 222–229.
- [29] L.P. Favero, P. Belfiore, *Manual de Análise de Dados*, Elsevier, Rio de Janeiro, 2017.
- [30] S. Lê, J. Josse, F. Husson, Principal component methods - hierarchical clustering - partitioning clustering: why would we need to choose for visualizing data?, *J. Stat. Software*, (2008) 1–17.
- [31] R Core Team, *R: A Language and Environment for Statistical Computing*, R Foundation for Statistical Computing, Vienna, Austria, 2020.
- [32] Z. Wang, H. Xie, J. Ren, Y. Chen, X. Li, X. Chen, T.-W.D. Chan, Metabolomic approach for rapid differentiation of *Fritillaria* bulbs by matrix-assisted laser desorption/ionization mass spectrometry and multivariate statistical analysis, *J. Pharm. Biomed. Anal.*, 185 (2020) 113177, <https://doi.org/10.1016/j.jpba.2020.113177>.
- [33] Y. Zhao, Y. Zhao, Y. Du, J.S. Kang, Characterization and classification of three common *Bambusoideae* species in Korea by an HPLC-based analytical platform coupled with multivariate statistical analysis, *Ind. Crops Prod.*, 130 (2019) 389–397.
- [34] R.O. Santos, B.M. Gorgulho, M.A. Castro, R.M. Fisberg, D.M. Marchioni, V.T. Baltar, Principal component analysis

- and factor analysis: differences and similarities in nutritional epidemiology application, *Rev. Bras. Epidemiol.*, 22 (2019) 1–14.
- [35] M.S.H. Bader, Sulfate removal technologies for oil fields seawater injection operations, *J. Pet. Sci. Eng.*, 55 (2007) 93–110.
- [36] I.T. Gabardo, E.B. Platte, A.S. Araujo, F.H. Pulgatti, Evaluation of Produced Water from Brazilian Offshore Platforms BT - Produced Water: Environmental Risks and Advances in Mitigation Technologies, K. Lee, J. Neff, Eds., Springer New York, New York, NY, 2011.
- [37] J. Neff, K. Lee, E. Deblois, Produced Water: Overview of Composition, Fates, and Effects, in: *Prod. Water Environ. Risks Adv. Mitig. Technol.*, Springer, New York, 2011.
- [38] P.J.C. Tibbetts, I.T. Buchanan, L.J. Gawel, R. Large, A Comprehensive Determination of Produced Water Composition, J.P. Ray, F. Rainer Engelhardt, *Produced Water: Technological/Environmental Issues and Solutions*, Springer US, Boston, MA, 1992.
- [39] G.F. da Cruz, A.J. Marsaioli, Processos naturais de biodegradação do petróleo em reservatórios, *Quim. Nova.*, 35 (2012) 1628–1634.
- [40] R.E. Chapman, ed., Chapter 9 – Origin and Migration of Petroleum: Geological and Physical Aspects, in: *Pet. Geol.*, Elsevier, Amsterdam, 1983, pp. 179–207.
- [41] R.F.R. Pereira, C.B. Vidal, A.C.A. de Lima, D.Q. Melo, A.N.S. Dantas, G.S. Lopes, R.F. do Nascimento, C.L. Gomes, M.N. da Silva, Chemometric characterization of alembic and industrial sugar cane spirits from cape verde and ceará, Brazil, *Int. J. Anal. Chem.*, 2012 (2012) 840528, doi: 10.1155/2012/840528.
- [42] F. Abreu, A. Sabariz, A. Quadro, A. Bueno, Avaliação da resistência à corrosão da liga de alumínio 6101 após diferentes tratamentos térmicos de precipitação, *Corros. Prot. Mater.*, 31 (2012) 65–70.
- [43] E.V. Dantas, Tratamento de água de refrigeração e caldeiras, José Olympo, Rio de Janeiro, 1988.
- [44] V. Gentil, *Corrosão*, 3ª, LTC, Rio de Janeiro, 1996.
- [45] D. Ribeiro, *Corrosão e Degradação em Estruturas de Concreto*, 2ª, GEN LTC, 2018.
- [46] X. Lu, L. Wang, L.Y. Li, K. Lei, L. Huang, D. Kang, Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China, *J. Hazard. Mater.*, 173 (2010) 744–749.