Acetate in formation waters at the southeast of the Maracaibo basin

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Introduction

Anions of carboxylic acids (AAC) can be present in high concentrations in oilfields, constituting 99% of the alkalinity reported in some formation waters (Kharaka y Harnor, 2003). Their presence is not detected since generally the most abundant of all carboxylic anions, acetate anion has an equivalent point similar to bicarbonate anion. This is why it is wrongly assumed that the alkalinity is provided exclusively by carbonate and bicarbonate anions when determined by titration method.

An over-estimation of bicarbonate values in water alters the results of geochemical modeling of water for prediction of formation damage by clogging or carbonate scales, estimating support for water injection secondary recovery processes and estimation of fouling behavior of produced waters intended for reuse (Zhang y Dawe, 1995; Kharaka y Harnor, 2003; Cantucci et al. 2009).

Additionally, the action of organic acids as ligands has important implications in the reactive metal transport (Fein, 1991).

Experimental

Five producers oil wells were selected in a depth range from 4734 m to 5444 m and temperatures between 96°C and 120°C with water cut higher to 30% depending on their potential to present organic anions dissolved in water.

Cations: sodium, potassium, calcium and magnesium and anions chloride, bromide, sulfate, carbonate, bicarbonate, acetate and formiate were determined. For cation analysis was prepared 20 mL aliquot of each sample. Prior to analysis these samples were filtered using 0.20 µm pore Teflon membranes, in order to exclude colloidal species.

Ca, Mg, Na and K were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) technique with a Teledyne Prodigy equipment.

Analyses of carbonate and bicarbonate were performed according to titration technique, during the first 72 hours. Titrations were carried out with sulfuric acid (Hach standardized 0.16 N) and phenolphthalein and bromocresol green indicators (Hach).

Chloride, bromide, sulfate, acetate and formiate anions were analyzed from an aliquot of 20 mL of each sample, previously filtered using 0.45 µm pore Teflon membrane and analyzed by liquid chromatography using a DIONEX equipment ICS-3000 with a 4 x 250mm IonPac AS18 column and KOH as mobile phase with gradient concentration. The amperage was modified of 120mA to 15mA specifically for the detection of formiate and acetate.

Results and Discussions

The five waters are considered Na-HCO3 type as is shown in Figure 1 (a). This however, would be different when discriminating the contribution to alkalinity by carboxylic acid anions, see Figure 1 (b), given that the determination of bicarbonate anion using the titration technique is indirect and does not allow distinguish between the equivalence point of bicarbonate and acetate.

As shown in Figure 1, acetate is one of the major anionic...
Carboxylic acid anions acetate and formiate contribute between 48 and 70% of total alkalinity for the 5 wells tested.

The determination of the anions of organic acids in petroleum reservoirs at temperatures between 80 °C and 160 °C is important because its estimate allows a better understanding of processes as mineral dissolution and precipitation, affecting models of porosity and permeability of the reservoir.

This leads to better predictive models of the behavior of the water, which in turn allow better management of reservoir productivity and produced water management.

Acknowledges
Authors want to thanks PDVSA Occidente for its support during sample collection.

References