

**Corrosion control  
using hydroxide and  
bicarbonate  
alkalising agents**

P. Torres-Lozada et al.

This discussion paper is/has been under review for the journal Drinking Water Engineering and Science (DWES). Please refer to the corresponding final paper in DWES if available.

# Corrosion control using hydroxide and bicarbonate alkalising agents in water drinking processes

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Received: 30 December 2014 – Accepted: 16 February 2015 – Published: 24 March 2015

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Published by Copernicus Publications on behalf of the Delft University of Technology.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## Abstract

The water supply industry is faced with three phenomena of great importance: the aggressiveness, corrosion, and incrustation of water distribution systems (WDS), which are primarily due to the low alkalinity of water sources and the addition of chemicals used in water treatment processes, which require pH adjustments during the last stage of the treatment process before going into the WDS. This article presents the results of using  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  with doses between 2 and  $20 \text{ mg L}^{-1}$  and  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  between 10 and  $250 \text{ mg L}^{-1}$  to adjust the pH of water treated from the Cauca River, which is located in Cali, Colombia, using stabilisation indices normally used in water treatment plants for pH monitoring processes and to better predict the behaviour of water in the WDS. The results indicate that for the case of the surface water source studied, which exhibits low alkalinity levels, the evaluated alkalisating agents, with the exception of  $\text{NaHCO}_3$ , can create conditions that lead to the precipitation of a protective calcium carbonate film. Because the pH values that guarantee an adequate pH adjustment are higher (8.7–9.0) than those specified by the Colombian water code and because other international rules indicate that these values do not compromise the health of consumers, it is advisable to review and adjust the code in this respect.

## 1 Introduction

When treating water to make it potable, the processes of coagulation and disinfection reduce alkalinity and pH (WHO, 2011), which makes it necessary to equilibrate the chemical balance of water at the end of the treatment to reduce its corrosive capacity and ensure that no encrustations are formed, which can cause reduction in the flow section (Barid, 2004; Casey, 2009). These situations have economic, hydraulic, aesthetic, and public health repercussions, which include water leaks, increased pumping costs, and deterioration of water quality in WDSs (Volk et al., 2000; Gray, 2008).

DWESD

8, 53–76, 2015

## Corrosion control using hydroxide and bicarbonate alkalisating agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



For the pH adjustment process, there are several alkalisng agents in use, which include strong base neutralisation (hydrated lime ( $\text{Ca}(\text{OH})_2$ ) and sodium hydroxide ( $\text{NaOH}$ )) and neutralisation with an alkaline carbonate (sodium carbonate and bicarbonate ( $\text{Na}_2\text{CO}_3$ ;  $\text{NaHCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ )). Furtado et al. (2011) found that  $\text{Ca}(\text{OH})_2$  and  $\text{NaHCO}_3$  are effective compounds to increase the alkalinity, whereas  $\text{Na}_2\text{CO}_3$ , although it raises the pH, is not as effective in that regard.

One technique to evaluate the pH adjustment process is to use stabilisation indices, where the most widely used are those that indicate water saturation, such as the  $\text{CaCO}_3$  Langelier saturation index (LSI), McCauley's driving force index (DFI),  $\text{CaCO}_3$  precipitation potential (CCPP), and those that depend on the type of piping, i.e., the aggressive index (AI), Larson-Skold index (LKI) and Ryznar stability index (RSI) (Schock, 2002; Imran et al., 2005; Trujillo et al., 2008; De Moel et al., 2013). However, authors such as Varó Galván et al. (2004) have indicated that there is still no index available that is universally applicable, which requires analysing the treatment process using several indices to determine the appropriate conditions for each WDS.

By applying stabilisation indices, this study evaluated the influence of alkalisng agents (hydrated lime, sodium hydroxide, sodium bicarbonate and sodium carbonate) on controlling corrosion in water treated from the Cauca River, which supplies a high percentage of the water for the city of Cali, Colombia.

## 2 Materials and methods

The study was conducted in the Puerto Mallarino water treatment plant (WTP) in the city of Cali, which treats raw water from the Cauca River. The following are the stages developed in this study: evaluate the effects of adding chemicals used in water treatment processes on the water's pH and total alkalinity and evaluate the pH adjustment using different alkalisng agents.

## 2.1 Evaluation of the effect of adding chemicals used in water treatment processes on pH and total alkalinity

Historical daily information was gathered and processed during the year 2012, which is available from EMCALI EICE ESP, regarding the raw water turbidity from the Cauca River and its relationship and effect on the dosage of the chemical products used during water treatment processes (coagulant, adsorbent, disinfectant, and alkalising agent) and on the total alkalinity ( $\text{mg CaCO}_3 \text{ L}^{-1}$ ) and pH in the water after it has been cleared, filtered, and treated.

## 2.2 Evaluation of the pH adjustment with different alkalising agents

### 2.2.1 Comparative analysis of alkalising agents

By means of a bibliographical review, a comparative analysis was conducted on the alkalising agents with the most widespread application, such as hydrated lime, sodium hydroxide, sodium bicarbonate, sodium carbonate, and calcium carbonate. The primary characteristics of each alkalising agent were grouped into three categories: technical aspects, occupational health, and economics, leading to a selection of the alkalising agents to be evaluated at the laboratory scale with treated water from the Cauca River.

### 2.2.2 Laboratory-scale evaluation of alkalising agents

For the pH adjustment, hydrated lime ( $\text{Ca(OH)}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were evaluated using 4% concentration solutions. According to Bueno-Zabala et al. (2014), to generate oversaturation conditions that allow for precipitation of the calcium carbonate film for the treated water from the Cauca River, it is necessary for the pH at the end of the process to exceed the saturation pH (pHs), which is between 8.7–9.0. For that reason, the

## Corrosion control using hydroxide and bicarbonate alkalising agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







tection Association) as very dangerous because it liberates heat when reacting with water, which can lead to combustion of materials in contact or close by, such as paper, fabric, cardboard, etc. (Calidra, 2007).

NaOH is easy to handle because its high solubility achieves good mixtures, avoids encrustations or increased turbidity in the final water, and is easy to acquire nationally. In addition, it has a high percentage of the active ingredient as a raw material, which is expensive (Sallanko et al., 2013). In terms of occupational health, NFPA 704 classifies it as very dangerous because it is highly corrosive and may cause severe burns, which requires special care for storage, specifically the need to use high-density polyethylene materials and precautions in electric power transmission lines due to the possibility of generating flammable hydrogen (GQ, 2006; Kim et al., 2008; Vargas et al., 2009).

NaHCO<sub>3</sub> is easy to handle given that it is more soluble at temperatures greater than 28 °C, where it behaves as sodium carbonate; it is widely available nationally, has a high percentage of active content, and is inexpensive as a raw material (Berrenechea, 2004; GQ, 2006; Ebbing and Gammon, 2010). Although it is harmless in terms of occupational health, even when present at high levels (Takasaki and Yamada, 2007), it may be necessary to mix it with Ca(OH)<sub>2</sub> or NaOH to adjust the pH in the case when a pH > 8 is required because it is a product that gradually changes the water's equilibrium (Kim et al., 2008; Casey, 2009). As a result, its application is recommended in small-scale plants or when Ca(OH)<sub>2</sub> creates problems (GQ, 2006; Casey, 2009).

Na<sub>2</sub>CO<sub>3</sub>, as NaHCO<sub>3</sub>, is easy to handle and must be used with another alkalisng agent primarily because of its high cost in the market and the addition of unwanted cations in the water (Manharawy and Hafez, 2002; Colindres, 2010). Na<sub>2</sub>CO<sub>3</sub> has a high content of active ingredient and its availability is limited. In addition to being imported, it is a nationally controlled substance (CNE, 1987; Di Bernanrdo and Sabogal, 2008; Birhnack et al., 2011). The NFPA 704 classifies it as dangerous, which requires specialised materials for handling (Hilleboe, 2000; Kim et al., 2008).

CaCO<sub>3</sub> is primarily used in countries such as Mexico, Ecuador, Argentina, and Brazil, which incurs additional costs from importing. This product has a high active content,

## DWESD

8, 53–76, 2015

### Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and the NFPA 704 classifies it as slightly dangerous; however, being less soluble than  $\text{Ca}(\text{OH})_2$ , it requires previous acidification in water with  $\text{CO}_2$ , which must remain for at least 15 min in a reactor, and another alkalisng agent must be added to reach adequate pH values (Birhnack et al., 2011; Lehmann et al., 2013).

Although the analysed products have the potential of being used in pH stabilisation processes, their selection depends on the different factors mentioned previously and on aspects such as the characteristics of the raw water, type of treatment processes previously used, availability at the site, etc. For this reason,  $\text{CaCO}_3$  was not evaluated in this study, given its limitations such as requiring added  $\text{CO}_2$  and importation of the product.

### 3.2.2 Laboratory-scale evaluation of the alkalisng agents

Figure 2 shows the behaviour of the alkalisng agents evaluated with respect to total alkalinity and final pH of the treated water from the Cauca River.

According to Fig. 2, strong bases increase total alkalinity values and pH with low doses, whereas salts require higher doses, which agrees with the results reported by De Sousa et al. (2010). However, strong bases do not provide the minimum alkalinity required for maintaining a buffer capacity in the WDS (approximately  $40 \text{ mg CaCO}_3 \text{ L}^{-1}$ ) due to their chemical reactions (Birhnack et al., 2011).

In terms of final pH, the only alkalisng agent that did not achieve the minimum pH ( $\text{pH} = 8.7\text{--}9.0$ ) to create the tendency of precipitating a calcium carbonate film was  $\text{NaHCO}_3$  because the maximum pH that was reached was 8.0.  $\text{NaCO}_3$  achieved the required values for both total alkalinity and minimum pH, though requires doses larger than  $130 \text{ mg L}^{-1}$ , which could lead to problems in dosage and storage depending on the volume of water to be stabilised (Dongchan et al., 2008).

Figure 3 shows the behaviour of the alkalisng agents evaluated through the indices that exhibit the tendency to precipitate calcium carbonate (LSI, DFI, and CAPP) and those that are used depending on the type of piping (AI, LKI, and RSI). It can be seen that all alkalisng agents, except for  $\text{NaHCO}_3$ , exhibit conditions that favour the ten-

## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





dency to precipitate calcium carbonate in the WDS given that the evaluated doses show results of oversaturated water and obtained pH values that exceeded the pHs.  $\text{NaHCO}_3$  does not achieve this because the final pH oscillates between 7–8.3 because the bicarbonate ions generally remain in that range within the carbonate system (Ebbing and Gammon, 2010; Birnhack et al., 2011).

With respect to the indices that apply to specific types of piping materials in the WDS, such as AI for asbestos cement piping, i.e., AC (31.9% of the city of Cali's WDSs is made of AC and is also the oldest), it can be seen that all the alkalisng agents, with the exception of  $\text{NaHCO}_3$ , allow for obtaining water with non-aggressive tendencies due primarily to the fact that the pH values of the water exceed the pHs.

For the LKI index applied to metallic piping (11.5% of the city of Cali's WDSs), only  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  resulted in a slight to small potential for corrosion with doses greater than  $200 \text{ mg L}^{-1}$  because they generate a total alkalinity greater than  $50 \text{ mg CaCO}_3 \text{ L}^{-1}$  (Agatemor and Okolo, 2008; Trujillo et al., 2008). For the RSI applied for steel piping (1.2% of the city of Cali's WDSs), it was found that no alkalisng agent would generate encrustation conditions, and although  $\text{Na}_2\text{CO}_3$  exhibits conditions close to equilibrium with doses of  $250 \text{ mg L}^{-1}$ , it would exceed Resolution 2115/2007 in terms of total alkalinity and pH.

Regarding the use of products containing sodium ( $\text{Na}^+$ ), it is advisable to control their concentration in water. The WHO (2011) recommends a concentration of less than  $200 \text{ mg L}^{-1}$  because it may generate rejection by users due to causing flavour problems of the water; the concentrations obtained in this study did not exceed this value ( $3.0\text{--}92.6 \text{ mg Na}^+ \text{ L}^{-1}$ ).

Table 5 shows certain international guidelines and rules in addition to the Colombian code for the operation conditions in terms of doses, pH, and total alkalinity in accordance with the optimum results of pH stabilisation indices, LSI, DFI, CCP, and AI, for the alkalisng agents evaluated, with the exception of  $\text{NaHCO}_3$  because it was the only one that did not obtain adequate pH adjustment conditions.

## DWESD

8, 53–76, 2015

### Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

⏴

⏵

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The results in Table 5 show that in terms of application dose,  $\text{Ca}(\text{OH})_2$  would require the least amount of raw material to obtain optimum results during the pH adjustment process, followed by NaOH and  $\text{Na}_2\text{CO}_3$ ; however, the latter requires doses greater than  $130\text{ mg L}^{-1}$ , which could lead to dosage problems (Dongchan et al., 2008). To

5 select an alkalising agent, one must take into account each of the agents' limitations because in general,  $\text{Ca}(\text{OH})_2$  exhibits low solubility problems in water, NaOH requires more complex storage conditions, and  $\text{Na}_2\text{CO}_3$  is a controlled substance in Colombia (Vargas et al., 2009; Labiod and Ghizellaoui, 2012; Sallanko et al., 2013).

As the main variable in the stabilisation process, pH must be controlled to reduce

10 corrosion in the WDS to a bare minimum, which avoids possible water contamination due to metal dissolution and adverse effects in appearance and flavour (Tam and Elefsiniotis, 2009; Wilczak et al., 2010; WHO, 2011).

One aspect of these results that should be highlighted is that the current Colombian code does not allow for adequate conditions to be obtained to remove the calcium

15 carbonate film in Cali's WDSs, which is primarily due to the pH limitation because getting good results requires the pH to exceed the pHs, which is between 8.7–9.0, a range that is at the upper bound of Resolution 2115/2007. However, the fact that other countries, such as Brazil, the European Union, and the United Kingdom, allow maximum values of  $\text{pH} > 9.0$  to reduce the effect of corrosion in WDSs (Hamdy et al.,

20 2011; Rout et al., 2014) leads us to recommend a review of this rule.

The value of alkalinity at the end of the stabilisation process for treated water from the Cauca River should be at a minimum range, between  $27.3\text{--}36.7\text{ mg CaCO}_3\text{ L}^{-1}$  (Bueno-Zabala et al., 2014), which is in accordance with recommendations in the literature (between  $40\text{ and }80\text{ mg CaCO}_3\text{ L}^{-1}$ ) to precipitate a calcium carbonate film in the

25 WDS (Berghult et al., 1999; Imran et al., 2005). Although  $\text{Ca}(\text{OH})_2$  and NaOH rapidly increase pH, they do not achieve adequate alkalinity results that provide a greater capacity to neutralise acids and avoid pH reductions in the WDS; in contrast,  $\text{Na}_2\text{CO}_3$  reaches the desired total alkalinity values but requires greater doses due primarily





**Corrosion control  
using hydroxide and  
bicarbonate  
alkalising agents**

P. Torres-Lozada et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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- 30

## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Tam, Y. S. and Elefsiniotis, P.: Corrosion control in water supply systems: effect of pH, alkalinity, and orthophosphate on lead and copper leaching from brass plumbing, *J. Environ. Sci. Heal. A*, 44, 1251–1260, 2009.

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## Corrosion control using hydroxide and bicarbonate alkalis agents

P. Torres-Lozada et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Table 1.** Test variables.

Variable	Units	Reference technique <sup>a</sup>
pH	–	4500-H <sup>+</sup> B
Total alkalinity	mg CaCO <sub>3</sub> L <sup>-1</sup>	2320-B
Total hardness	mg CaCO <sub>3</sub> L <sup>-1</sup>	2340 C
Calcic hardness	mg CaCO <sub>3</sub> L <sup>-1</sup>	2340 C
Calcium	mg Ca <sup>2+</sup> L <sup>-1</sup>	3500-Ca D
Sodium	mg Na <sup>+</sup> L <sup>-1</sup>	3500-Na B
Temperature	°C	2550-B
Turbidity	UNT	2130-B
Chlorides	mg Cl <sup>-</sup> L <sup>-1</sup>	4500-Cl <sup>-</sup> B
Sulphates	mg SO <sub>4</sub> <sup>2-</sup> L <sup>-1</sup>	4500-SO <sub>4</sub> <sup>2-</sup> E

<sup>a</sup> APHA et al. (2005).

## Corrosion control using hydroxide and bicarbonate alkalis agents

P. Torres-Lozada et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Table 2.** Indices with the greatest applicability in controlling the pH stabilisation process: tendency towards precipitation  $\text{CaCO}_3$ .

Index	Equation
Langelier Saturation Index (LSI)	$\text{LSI} = \text{pH} - \text{pH}_s \quad (1)$ <p>Where: pH at the site; <math>\text{pH}_s</math>: saturation pH            Interpretation: LSI &gt; 0, oversaturated; LSI = 0, saturated;            LSI &lt; 0, unsaturated            Characteristic: Indicator for conditions of precipitation of <math>\text{CaCO}_3</math></p>
McCaughey Driving force Index (DFI)	$\text{DFI} = \frac{[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]}{K_s 10^{10}} \quad (2)$ <p>Where: <math>[\text{Ca}^{2+}]</math>: Calcium in <math>\text{mg CaCO}_3 \text{ L}^{-1}</math>; <math>[\text{CO}_3^{2-}]</math>: Carbonate concentration; <math>K_s</math>: Solubility product of <math>\text{CaCO}_3</math>            Interpretation: DFI &gt; 1, oversaturated; DFI = 1, saturated;            DFI &lt; 1, unsaturated            Characteristic: Measures the tendency to deposit a <math>\text{CaCO}_3</math> film</p>
Calcium Carbonate Precipitation Potential (CCPP)	$\text{CCPP} = \text{Alk}_i - \text{Alk}_{\text{eq}} \quad (3)$ <p>Where: <math>\text{Alk}_i</math>: Initial alkalinity; <math>\text{Alk}_{\text{eq}}</math>: Equilibrium alkalinity            Interpretation: CCPP &gt; 0, oversaturation and <math>\text{mg CaCO}_3 \text{ L}^{-1}</math> that must be precipitated; CCPP &lt; 0, unsaturation and <math>\text{CaCO}_3</math> that dissolve            Characteristic: Indicates the theoretical approximate mass of <math>\text{CaCO}_3</math> that could be precipitated in the piping</p>

Source: Schock (2002), Varó Galván et al. (2004), APHA et al. (2005), Imran et al. (2005), Trujillo et al. (2008), De Sousa et al. (2010), De Moel et al. (2013), Bueno-Zabala et al. (2014).

**Table 3.** Indices with the greatest applicability in controlling the pH stabilisation process: type of piping.

Index	Equation
Aggressive Index (AI)	$AI = pH + \log(AH) \quad (4)$ <p>Where: pH: Hydrogen ion potential; A: Total alkalinity; H: Calcium hardness            Interpretation: AI &lt; 10, very aggressive; 10 &lt; AI &lt; 12, moderately aggressive; AI &gt; 12, not aggressive            Characteristic: Estimates the tendency of water to deteriorate the asbestos cement piping structure</p>
Larson-Skold Index (LKI)	$LKI = \frac{[Cl^-] + 2[SO_4^{2-}]}{[HCO_3^-]} \quad (5)$ <p>Where: Cl<sup>-</sup>: Chlorides (molL<sup>-1</sup>); SO<sub>4</sub><sup>2-</sup>: Sulphates (molL<sup>-1</sup>); HCO<sub>3</sub><sup>-</sup>: Bicarbonates (molL<sup>-1</sup>)            Interpretation: results represented in corrosion potential: &lt; 0.2, does not exist; 0.2–0.4, small; 0.4–0.5, slight; 0.5–1.0, average; &gt; 1, Strong            Characteristic: Represents the corrosiveness due to chloride and sulphate ions. Applied in metallic piping and waters with medium to high alkalinity (&gt; 50 mg CaCO<sub>3</sub> L<sup>-1</sup>)</p>
Ryznar Stability Index (RSI)	$RSI = 2pH_s - pH \quad (6)$ <p>Where: pH at the site; pH<sub>s</sub>: saturation pH            Interpretation: RSI &lt; 6.5, causes encrustation; 6.5 &lt; RSI &lt; 7, close to equilibrium; RSI &gt; 7, corrosive            Characteristic: Determines the corrosive or encrustation character of water. Applies to steel piping and water with medium to high alkalinity (&gt; 50 mg CaCO<sub>3</sub> L<sup>-1</sup>)</p>

Source: Schock (2002), Varó Galván et al. (2004), APHA et al. (2005), Imran et al. (2005), Trujillo et al. (2008), De Sousa et al. (2010), De Moel et al. (2013), Bueno-Zabala et al. (2014).

**Corrosion control using hydroxide and bicarbonate alkalisng agents**

P. Torres-Lozada et al.

[Title Page](#)

[Abstract](#) | [Introduction](#)

[Conclusions](#) | [References](#)

[Tables](#) | [Figures](#)

[⏪](#) | [⏩](#)

[◀](#) | [▶](#)

[Back](#) | [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Corrosion control using hydroxide and bicarbonate alkalis**

P. Torres-Lozada et al.

**Table 4.** Technical, occupational health, and economic aspects of the alkalis used in pH adjustment.

Characteristic	Alkalis agent					
	Hydrated lime Ca(OH) <sub>2</sub>	Sodium hydroxide NaOH	Sodium bicarbonate NaHCO <sub>3</sub>	Sodium carbonate Na <sub>2</sub> CO <sub>3</sub>	Calcium carbonate CaCO <sub>3</sub>	
Technical	Chemistry	Strong base		Salt		
	Total alkalinity contribution (as CaCO <sub>3</sub> )	1.35	1.25	0.60	0.94	1.00
	Buffer capacity contribution	0 equivalent	0 equivalent	1 equivalent HCO <sub>3</sub> <sup>-</sup>	2 equivalent CO <sub>3</sub> <sup>2-</sup>	2 equivalent CO <sub>3</sub> <sup>2-</sup>
	Storage	Simple	Specialised	Simple		
	Dosage	Complex (Lime slacking, encrustations)	Easy (Does not form insoluble salts)	Medium complexity (Mix with bases and addition of unwanted cations in the water)	Complex (Acidify with CO <sub>2</sub> combination with another alk.)	
Occupational Health	NFPA 704 Evaluation - National Fire Protection Association (Scale 0: Minimum; 1: Slight; 2: Moderate; 3: Serious; 4: Severe)		Occupational Health			
	CaO: 3 (Very dangerous) Slaked lime: 1 (Slight danger)	3 (Very Dangerous)	0 (No risk)	2 (Dangerous)	1 (Slightly dangerous)	
	Flammability					
	0 (Does not ignite)					
	Reactivity					
	0 (Stable)	1 (Unstable in case of heating)	0 (Stable)			
Economic	Easy to acquire in Colombia	Yes	Yes – Controlled in Colombia		No but it is in Mex., Ecu., Arg., Bras.	
	Solubility (g prod./100 mL water) 20 °C	0.2	111	9.6	7,1–10	0.0014
	% Available active content	CaO: Min. 90% Slaked lime: 75–84%	99–100%	98–100%	98–99%	95–99%
	Raw material cost <sup>a</sup> (COP\$ kg <sup>-1</sup> w/o tax)	CaO: 336 Slaked lime: 475	1050	31.2	900 <sup>b</sup>	80 (0.04US) <sup>b</sup>

<sup>a</sup> Final cost should include raw material cost, dosage, and buffer capacity.

<sup>b</sup> Transportation not included.

Source: Kim et al. (2008), Colindres (2010), Ebbing and Gammon (2010), Birnhack et al. (2011), Lehmann et al. (2013).

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

⏴ ⏵

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



**Table 5.** Operation conditions and results of pH stabilisation with different alkalisng agents.

Parameter	Alkalisng agents			Code	
	Hydrated lime	Sodium hydroxide	Sodium carbonate	National (Res. 2115/07)	International
Dose (mgL <sup>-1</sup> )	6–8	8–10	130–200	–	–
pH (–)	8.8–9.3	9.1–9.4	8.6–9.0	6.5–9.0	6.0–9.5 <sup>a</sup> 6.5–9.5 <sup>b</sup> 6.5–10.0 <sup>c</sup>
Total alkalinity (mg CaCO <sub>3</sub> L <sup>-1</sup> )	14–16	16–19	85–125	200	–

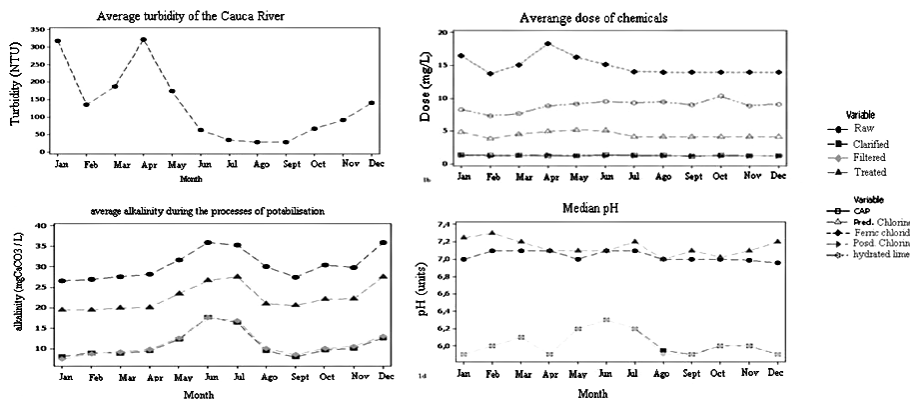
<sup>a</sup> Brazil, PORTARIA No. 518/2004.

<sup>b</sup> Unión European, Directive 98/83/CE.

<sup>c</sup> England and Wales, No. 3911/2001 (W.323)

## Corrosion control using hydroxide and bicarbonate alkalisng agents

P. Torres-Lozada et al.



**Figure 1.** Turbidity behaviour of the Cauca River, chemical doses, and their effect on alkalinity and pH during the water treatment processes. Historical daily data for the year 2012.

[Title Page](#)

<a href="#">Abstract</a>	<a href="#">Introduction</a>
<a href="#">Conclusions</a>	<a href="#">References</a>
<a href="#">Tables</a>	<a href="#">Figures</a>

⏪
⏩
  
⏴
⏵

<a href="#">Back</a>	<a href="#">Close</a>
----------------------	-----------------------

[Full Screen / Esc](#)

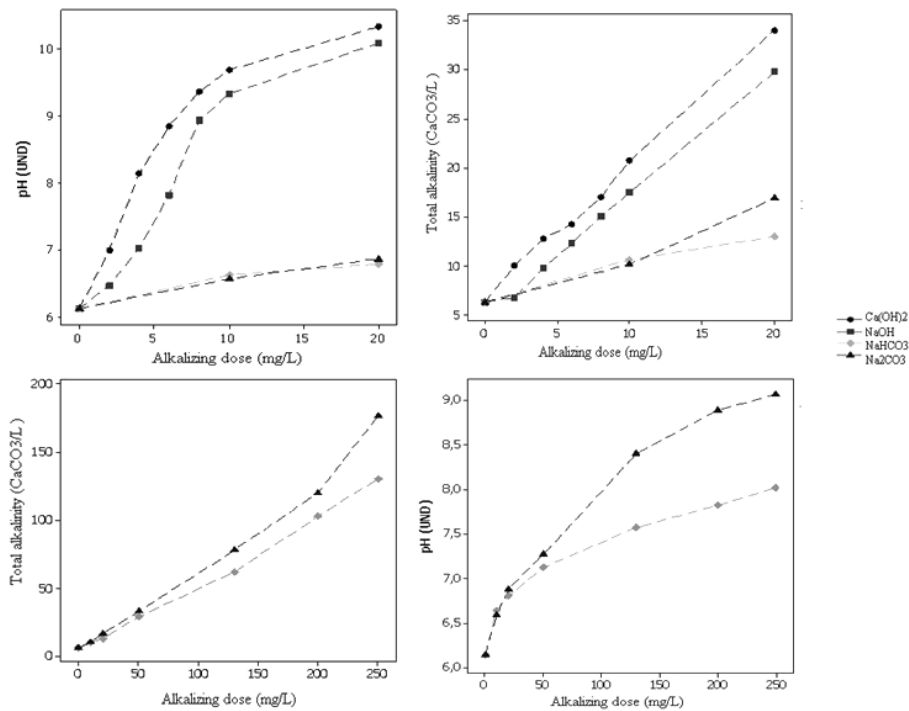
[Printer-friendly Version](#)

[Interactive Discussion](#)



## Corrosion control using hydroxide and bicarbonate alkalis agents

P. Torres-Lozada et al.



**Figure 2.** Effect of different alkalis agents on total alkalinity and pH for the evaluated doses.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

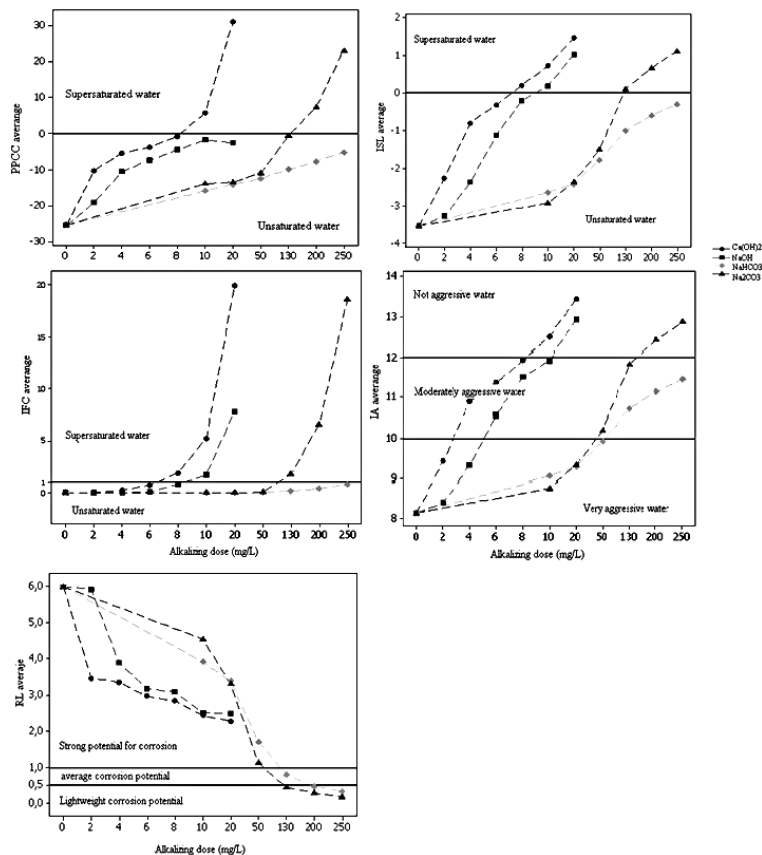
[Printer-friendly Version](#)

[Interactive Discussion](#)



## Corrosion control using hydroxide and bicarbonate alkalis agents

P. Torres-Lozada et al.



**Figure 3.** LSI, DFI, CCPP, AI, LKI, and RSI indices for hydrated lime, sodium hydroxide, sodium bicarbonate, and sodium carbonate.

[Title Page](#)  
[Abstract](#)   [Introduction](#)  
[Conclusions](#)   [References](#)  
[Tables](#)   [Figures](#)  
⏪   ⏩  
⏴   ⏵  
[Back](#)   [Close](#)  
[Full Screen / Esc](#)  
[Printer-friendly Version](#)  
[Interactive Discussion](#)

