

CHARACTERIZATION OF DEPOSITS FORMED IN A WATER DISTRIBUTION SYSTEM

CARACTERIZACIÓN DE DEPÓSITOS FORMADOS EN UN SISTEMA DE DISTRIBUCIÓN DE AGUA POTABLE

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RESUMEN

La aparición de depósitos indeseados en cualquier sistema de distribución de agua potable es inevitable en condiciones normales de operación. Conocer la naturaleza de tales depósitos ayudará a establecer las causas de su formación y, en consecuencia, a mantener altos niveles de calidad del agua. En este trabajo se presentan los resultados de un amplio estudio realizado en el sistema de distribución de agua de una ciudad situada en una zona tropical. La caracterización de los depósitos obtenidos en diferentes sitios a lo largo del sistema se realizó mediante Espectroscopia Infrarroja (IR), Difracción de Rayos X (DRX), Energías Dispersivas de Rayos X (EDS) y Microscopia Electrónica de Barrido (MEB). El análisis de las muestras indica la presencia de tres tipos predominantes de depósitos: depósitos color marrón, tubérculos y depósitos blancos. Se halló que los primeros están constituidos principalmente por aluminosilicatos y ácidos húmicos. Los tubérculos se componen principalmente de mezclas de magnetita, goethita y, en algunos casos, lepidocrocita. Por su parte, los depósitos blancos están constituidos por calcita, aluminosilicatos y cuarzo. Además, se hallaron contenidos de materia orgánica y sólidos volátiles de $14.0 \pm 5.0\%$ para los depósitos marrón y de $11.2 \pm 2.0\%$ para los tubérculos.

Palabras clave: Depósitos, sistemas de distribución de agua, biopelículas, tubérculos, análisis fisicoquímicos.

ABSTRACT

The development of unwanted deposits in any water distribution system is unavoidable under standard conditions. Knowing the composition of such deposits will help to establish the causes of deposit formation and consequently to be able to keep water quality as high as possible. This paper presents the results of an extensive study of deposits found in a water distribution system of a tropical city. Characterization of materials collected across the system was made by infrared spectroscopy (IR), X ray diffraction (XRD), energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). Analysis of the samples taken at several sites of the system reveals the presence of three predominant deposits: a brown coloured deposit, tubercles and white deposits. Aluminosilicates and humic acids were found to be main constituents in brown deposits. Tubercles were mostly mixtures of magnetite, goethite and in some cases lepidocrocite. White deposits were formed by calcite, aluminosilicates and quartz. Organic matter as volatile solids were $14.0 \pm 5.0\%$ for brown deposits and $11.2 \pm 2.0\%$ for tubercles.

Keywords: Deposits, water distribution systems, biofilms, tubercles, physico-chemical analysis.

INTRODUCTION

A water distribution network can not be considered an inert system but a reactor interacting with the interior aqueous environment and one of the main consequences of such

interaction is the formation of unwanted deposits [1]. The main sources of deposits in water distribution systems are particulate matter transported by water, microbial activity and physicochemical reactions both at the water/pipe wall interface and within the water bulk [1-4].

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Water quality can be strongly affected by the existence of deposits [2,5]; release of corrosion products from iron alloys surfaces (steel and cast iron, mainly), may change colour, odour and taste [5-7]; interactions between biofilm, humic substances and iron oxide may negatively affect the microbiological quality of the water [8], promote the release of pathogenic microorganisms [2,9], cause a drastic reduction in the efficiency of disinfectants [2] and may also induce a chemical decay of the residual chlorine [5]. Ionic species coming either from the natural water source or from pipe scales have been found to be a probable cause of public health problems [10]. Additionally, deposit formation may drastically reduce the hydraulic capacity of pipelines due to the formation of tubercles [4].

Recent publications on the composition of deposits in potable water systems indicate that minerals, organic matter and bacterial biomass are the main constituents of drinking water deposits [1-2]. Morphology and composition of the corrosion products formed on the internal walls of ferrous pipelines have also been studied, revealing a strong influence of water quality on the characteristics of the developed material [6] and a direct correlation between composition of deposits and the bacterial species found [4].

In the present study an extensive physicochemical characterization of the deposits found inside the complex network of water mains in the city of Medellín was made, using several analytical techniques such as XRD, FTIR, SEM and EDS. Both inorganic and organic matter was found to make part of the deposits. The compounds forming the deposits are reported.

EXPERIMENTAL

The infrastructure studied forms part of the three major subsystems: Ayurá (A), Manantiales (B) and Villa-Hermosa (C). Although water is supplied to each plant from a separate dam, the treatment methods are quite similar in the three plants with small differences in residence times. In any case, the main substances added to the water are: aluminium sulphate during coagulation, hydrogen peroxide for manganese oxidation, lime for pH adjustment and gaseous chlorine. The pipeline network is mostly made of reinforced concrete (about 54%), ductile iron (about 27%) and steel (10%). Storage facilities are mainly made of reinforced concrete, and pipeline accessories of ductile iron and steel.

For each plant one sampling site, as close as possible to the plant exit, was selected. Additional sampling sites, in which water quality problems have been reported, were

selected as follows: two for the subsystems A and B and one for subsystem C, the smaller subsystem. Samples were taken from the interior of the pipeline network and from the inside of the nearest tank (see table 1). Deposit samples were collected randomly at each sampling site, using either a stainless steel or a plastic spatula for hard and soft deposits. Historic data (years 2000 to 2003) of water pH was provided by the service company; in addition water samples were taken at both the plant exit and a distant tank for each subsystem and analysed regarding free chlorine residuals.

Deposit samples were dried during 48 hours at 40°C. Then, samples were grinded using an agate mortar until approximately 98% passed a No. 325 mesh. XRD analyses were carried out in a Bruker AXS D8 Advance diffractometer. FTIR samples were prepared as KBr pellets and analysed in a Perkin-Elmer 1760 spectrometer. An ESEM Philips XL30, equipped with an EDS electronic microprobe was employed. Samples were also analysed regarding volatile and fixed solids.

Table 1. Sites selected for sampling of deposits in the main water network of Medellín city. Approximate pipeline age is reported. (P: pipeline, T: tank, ACCP: reinforced concrete pipes).

| Sub system | Sampling site | | Distance from plant (km) | Material | Age (y) |
|------------|---------------|---|--------------------------|----------|---------|
| | P | T | | | |
| A | X | | 3.2 | ACCP | 23 |
| | X | | 10.3 | ACCP | 22 |
| | | X | 10.3 | Concrete | 22 |
| | X | | 12.1 | ACCP | 20 |
| | | X | 12.1 | Concrete | 20 |
| B | X | | 1.9 | ACCP | 12 |
| | X | | 17.4 | ACCP | 10 |
| | | X | 17.4 | Concrete | 10 |
| | X | | 7.9 | ACCP | 30 |
| | | X | 7.9 | Concrete | 30 |
| C | X | | 0.2 | Steel | 40 |
| | X | | 0.9 | Steel | 40 |
| | | X | 0.9 | Concrete | 40 |

RESULTS AND DISCUSSION

Three main deposits were found across the water distribution system under study: a) *Brown deposits* formed everywhere in the system, b) *tubercle deposits* formed on metallic (steel and ductile iron) surfaces, and c) *white deposits*, found only at some places. Deposits with similar characteristics

to *brown and tubercle deposits* have been reported in other studies [8-9,11-12].

Figure 1 presents the typical IR spectra of the three main deposits and the corresponding results are resumed in table 2.

Electron microscopy analysis of *brown deposits* revealed a heterogeneous morphology and composition; main components in most samples are C, O, Al, Si, Mn, Fe, Ca and Mg (see table 3).

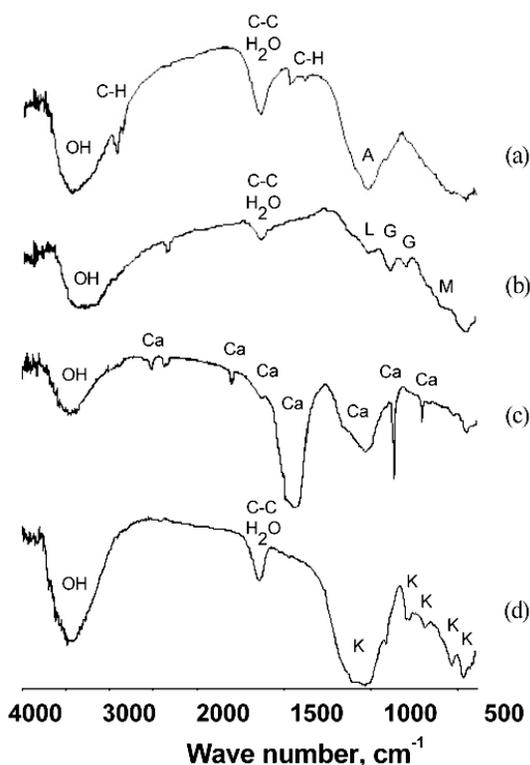


Figure 1. Infrared spectra of: (a) Brown deposit from shared part of the system. (b) Tubercle deposit from A subsystem. (c) White deposit from a metallic surface in C subsystem. (d) White deposit from a concrete surface in B subsystem (A: aluminium silicate hydroxides, Ca: calcium carbonate, L: lepidocrocite, G: goethite, M: magnetite, K: kaolin/smectite).

The results of SEM and EDS analysis indicate that *tubercle deposits* are morphologically and chemically homogeneous across the distribution system. A tubercle cross section micrograph (figure 2) clearly reveals the existence of three different parts: a hard shell in the middle of soft, loose inner and outer materials. However, no big differences in chemical composition were found by EDS analysis (see table 3).

White deposits showed no morphological distinctive characteristics and EDS analysis of a deposit collected from subsystem A revealed O and Al as major components whereas a similar deposit found in subsystem C is mainly made of C, O, Ca and Si.

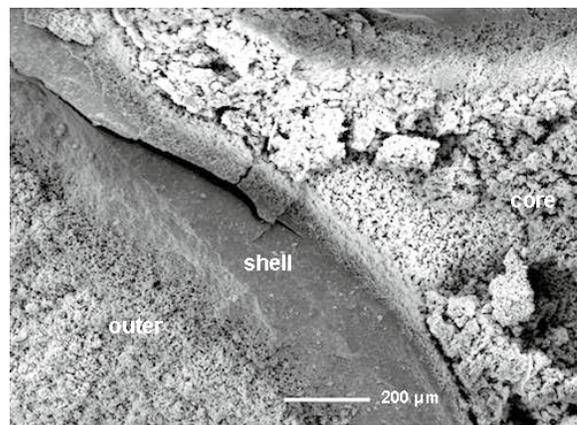


Figure 2. Cross section SEM micrograph revealing the three parts (core, compact shell and outer deposit) of a tubercle deposit. Accelerating voltage: 20 kV. Magnification: 80X.

Results of XRD analysis of *brown deposits* reveal important variations according to the colour intensity: Dark deposits appear to be amorphous whilst the lighter brown ones contain crystalline compounds, quartz as the main constituent mixed with an aluminium silicate hydroxide, most probably kaolinite. Similar compounds in potable water deposits were reported elsewhere [2,17]. *Tubercle deposits* formed at different sites in the water system showed mainly the presence of magnetite and goethite, with minor amounts of lepidocrocite (see figure 3a, 3b and 3c). Analysis of a brown deposit sample formed on a metallic surface (figure 3e) reveals mixtures of magnetite, goethite and kaolinite. XRD analysis of various *white deposits* reveals that soft material is made of varying amounts of quartz, calcite and basic aluminosilicates (see figure 3d) whilst the compact deposit is principally made of calcite.

The volatile solids (VS) content for *Brown deposits* indicates a median value of about 14.0% with a variation of $\pm 5.0\%$ for specimens collected at different sampling sites. *Tubercle deposits* show a slightly lower median value for volatile solids of about $11.2\% \pm 2.0\%$. Other researchers found VS values between 5.9 and 28% [1], from 7.4 to 23.5% [11], and from 14 to 24% [18]. Thus, VS contents obtained in the present study are relatively of the same magnitude of those obtained in different studies as well as the variations measured for the different sampling sites.

Table 2. Results of the analysis of the IR spectra of the different deposits found.

| Sample (spectrum) | Absorption frequency (cm ⁻¹) | Related compounds, groups or vibration | Reference |
|---------------------------------|--|---|-----------|
| Brown deposit (Figure 1a) | 3475, 1630, 1400, 1000 and 600 | Aluminosilicates | 13 |
| | 2950, 2880 and 1470 to 1380 | Organic matter (C-H vibration in CH ₃ or CH ₂ groups) | 14 |
| | 1630 | C-C vibration | |
| Tubercle deposit (Figure 1b) | 790 and 895 | Goethite | 13 |
| | 1020 | Lepidocrocite | |
| | 580 | Magnetite | |
| | 3187 | Vibrations of OH groups in goethite and the | 15 |
| | 3384 | Envelope of hydrogen-bonded surface OH groups | |
| | 1400 | Adsorbed carbonates | 16 |
| | 1630 | Water vibration | 15 |
| | C-C vibration | 14 | |
| White deposit (Figure 1c) | 2500, 1800, 1435, 870 and 710 | Calcite (calcium carbonate) | 13 |
| | 3425, 1630, 1140 and 1030 | Complex silicate, either containing water or hydroxide groups | |
| White deposit (Figure 1d) | 3425, 1639, 1100, 1030, 1000, 915, 781, 694, 533 and 462 | Phyllosilicate (kaolin/smectite) | |

Table 3. Most typical values of several samples of brown and tubercle deposits obtained from EDS analysis.

| Element | Brown deposits | | | Tubercle deposits | | |
|---------|----------------|---------------|---------------|-------------------|--------------|------|
| | Median at. % | Minimum at. % | Maximum at. % | Outer shell | Middle shell | Core |
| C | 11 | 8 | 37 | 9 | 6 | 7 |
| O | 59 | 47 | 63 | 60 | 58 | 53 |
| Al | 10 | 6 | 15 | | | |
| Si | 8 | 4 | 12 | 3 | 2 | 1 |
| Mn | 3 | 2 | 6 | | | |
| Fe | 2 | 1 | 13 | 28 | 30 | 38 |
| Mg | 1 | 1 | 3 | | | |
| Ca | 1 | 0 | 3 | | | |

Evidence of organic matter in the deposits is readily obtained from infrared results, in particular for *brown deposits* by the vibrations of CH₃ and CH₂ radicals at 2950, 2880 and 1380 to 1470 cm⁻¹. The variations in the intensity of these absorption bands from sample to sample can be explained by differences in the nature of organic matter in the various samples [1]. Although the band observed from 1380 to 1470 cm⁻¹, which is always observed in *brown deposits* spectra, may be also associated with mineral species; it becomes wider and less intense when the intensity of the peaks at 2950 and 2880 cm⁻¹ also decreases, revealing some relationship between these absorption bands.

Vibrations of amide species around 1650 and 1550 cm⁻¹ have been reported [11] as an indication of presence of biological material in a sample. However, the existence of inorganic material generates interference in that region [1,11], which is the case observed in this study. Consequently, for cases of deposits composed by mixtures of organic and inorganic matter a better indication of the presence of biofilm can be obtained from the absorption bands around 2950 and 2880 cm⁻¹. Comparing these bands for the different deposits it is concluded that volatile solids are associated to both organic and inorganic matter compounds as reported elsewhere [1]. It appears that organic matter in *brown deposits* is made of humic acids according to the FTIR spectra analysis [19]; these substances are readily found in natural water sources [20].

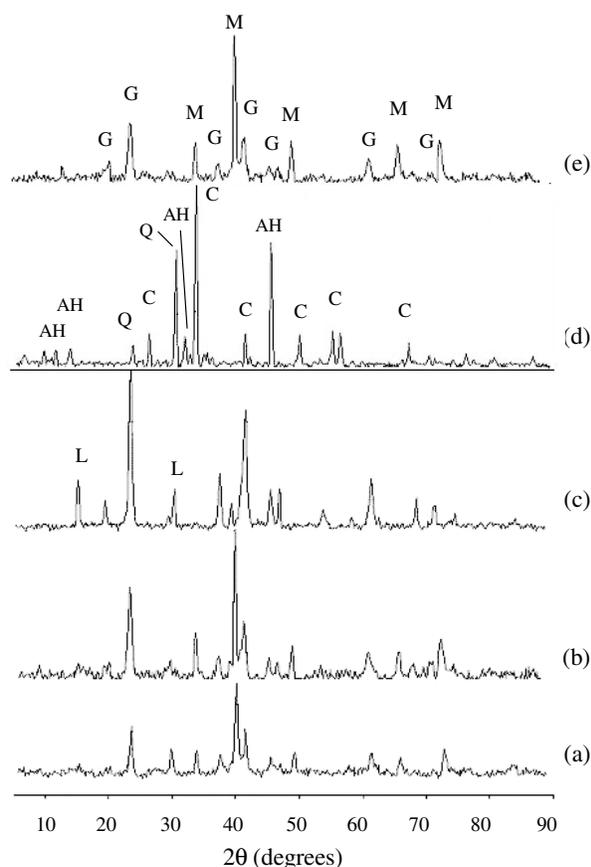


Figure 3. X-ray diffraction patterns of various samples: (a) Tubercle from A subsystem, (b) Tubercle from B subsystem, (c) Tubercle from C subsystem, (d) Soft white deposit from a tank at subsystem C and (e) Brown deposit formed on a metallic surface in B subsystem (G: goethite, M: magnetite, L: lepidocrocite AH: aluminium silicate hydroxides, C: calcite, Q: quartz).

With the information from the different analytical techniques it can be established that *brown deposits* are mainly composed by SiO_2 , $\text{Al}(\text{OH})_3$, MnO_2 , FeOOH , MgO and CaCO_3 plus organic compounds such as humic acids. Based in the EDS atomic values, the corresponding theoretical oxygen accounts for about 60 atomic percent closely resembling the value of about 59 atomic percent reported in table 3. *Tubercle deposits* are composed of magnetite, goethite and lepidocrocite as main constituents, in agreement the results reported by other researchers [6,21]. However, according to the sampling site location in the subsystem; plant exit, network or tank, goethite to magnetite ratios varies; goethite is more abundant in samples from inside tanks, whereas magnetite predominates in samples collected from other places. It has been reported that increasing the concentration of oxidants in water and

maintaining water flow might induce magnetite formation in the scales [6]. In addition, changes in the composition of *tubercle deposits* might be also related to the effect of pH and interactions with carbonate, chloride and sulphate; introduced at the treatment plant.

Analysis of historic data reveals that water pH values at plant exits are: 7.8 ± 0.3 for subsystem A, 7.9 ± 0.6 for subsystem B and 6.8 ± 0.4 for subsystem C. This data also indicates that water pH measured at tanks is nearly the same than at plant exit for subsystems B and C whereas for subsystem A it was 7.2 ± 0.5 . The formation of goethite and lepidocrocite is favoured in solutions with pH from 5 to 7, whilst pH values above 8 privilege magnetite formation [22]. Therefore, higher amounts of goethite and lepidocrocite will be expected to be found in *tubercle deposits* collected from subsystem C, while magnetite formation will more viable in subsystem B and at the plant exit of subsystem A; this is in good agreement with the XRD results (see figure 3). Free chlorine residuals at the plant exits is between 20 to 27% higher than at distant tanks; therefore, it might be possible, that high free chlorine residuals content in water favours the formation of magnetite over goethite, as observed in atmospheric corrosion [23]. In any case, higher amounts of magnetite in pipeline corrosion products reduce iron release into water [6,12]. In table 4, general conditions favouring either magnetite or goethite are presented.

Table 4. General conditions that favour the formation of magnetite or goethite and lepidocrocite in tubercle deposits.

| Higher magnetite content | Higher goethite and lepidocrocite content |
|-----------------------------|---|
| pH > 8 | pH 5-8 |
| Distribution system | Inside tanks |
| Higher water flow | Stagnant conditions |
| Higher chlorine content | Less chlorine content |
| Less carbonate ions content | Higher carbonate ions content |
| Less iron release to water | Higher iron release to water |
| Subsystem A, B | Subsystem C |

Magnetite formation is enhanced under the low oxidation conditions at the core of the tubercle [23]. Theoretical oxygen to iron ratios for goethite and magnetite are about 2.0 and 1.3, respectively; from table 3, these ratios are about 2.1, 1.9 and 1.4 for outer, shell and core materials, correspondingly. Microbial activity may also encourage magnetite formation inside the tubercle [21]; this is

supported by the morphology of the tubercle samples studied here [6,21]. *White deposits* were most probably formed as a result of sedimentation of suspended particles carried by the water flow [2,17] or by local changes of physico-chemical conditions [24,25].

CONCLUSIONS

The analysis of unwanted deposits on a water distribution system of a tropical city reveals the predominance of brown, tubercle and white deposits. Organic matter content measured as volatile solids (weight percent) was found to be around 11% for tubercles and 14 % for brown deposits.

Brown deposits principally contain aluminosilicates compounds, quartz and organic compounds, most probably humic acids. Tubercles are formed by electrochemical and microbiological activity; they are composed mainly of goethite and magnetite. Changes in the composition of tubercle samples might be related to the effect of pH and free chloride concentration. White deposits are composed of variable mixtures of calcite, quartz and aluminosilicates.

FTIR analyses could be used as an indication of the formation or presence of organic material in the sample, and therefore, as an indicator of the presence of biofilm. The presence of absorption bands around 2950 and 2880 cm^{-1} can be a good indication of the presence of the organic matter, and hence for biofilm, because these bands are not affected from interference from bands of inorganic material (silicates, hydroxides and carbonates).

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