Manganese micro-nodules on ancient brick walls

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Abstract

Romans, Jews, Arabs and Christians built the ancient city of Toledo (Spain) with bricks as the main construction material. Manganese micro-nodules (circa 2 μm in diameter) have grown under the external bio-film surface of the bricks. Recent anthropogenic activities, such as, industrial emissions, foundries or traffic and housing pollution have further altered these old bricks. The energy-dispersive X-ray microanalyses (XPS) of micro-nodules shows Al, Si, Ca, K, Fe and Mn, with some carbon species. Manganese atoms are present only as Mn^{4+} (pyrolusite phase, MnO_2) and iron as Fe^{3+} ($\text{FeOOH}\text{-Fe}_2\text{O}_3$ mixtures). The large concentration of algae biomasses of the River Tagus and the Torcón and Guajaraz reservoirs suggest manganese micro-nodules are formed either from water solutions rich in anthropogenic MnO_4K in a reduction environment (from Mn^{7+} to Mn^{4+}) or by oxidation mechanisms from dissolved Mn^{2+} (from Mn^{2+} to Mn^{4+}) linked to algae biofilm onto the ancient brick surfaces. Ancient wall surfaces were also studied by scanning electron microscopy (SEM-EDS) and X-ray diffraction (XRD). Chemical and biological analyses of the waters around Toledo are also analysed for possible sources of manganese. Pyrolusite micro-nodules on ancient brick walls are good indicators of manganese pollution.

Keywords: Heritage preservation; Brick alterations; manganese micro-nodules; biofilm; XPS, XRD, SEM-EDS.

1. Introduction

Manganese oxide minerals were used for thousands of years as pigments and to clarify glass. Nowadays ores of manganese metal serve as catalysts, and as material for batteries. Manganese nodules pave huge areas of the seabed and the bottom of many fresh-water lakes (Post, 1999). The presence of low levels of manganese element in reticular water precipitates manganese oxides on pipeline surfaces. In drinking-water distribution systems, sloughing of manganese oxide deposits results in brown-black, unpleasant-tasting water, which stains fixtures, equipment, swimming pools, and laundry. Most water authorities adhere to the World Health Organization recommended level of 0,05 mg/litter (Sly *et al.*, 1990). High manganese ratios in water are considered undesirable, because when water is exposed to air, Mn^{2+} oxides to Mn^{4+} and precipitates as manganese oxide. Current manganese removal methods generally require the use of strong oxidising agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide and ozone (Aziz and Smith, 1996).

High manganese amounts can also deteriorate construction materials; for instance, airborne pollutants harm buildings by both decay and staining (Massey, 1999). This author studied changes in urban air quality and their effects on buildings, vehicle pollution, and the processes involved in aqueous phase oxidation, stone porosities, humidity and oxidant compounds. Manganese sources stem from traffic in air pollution in urban areas (e.g., Wrobel *et al.*, 2000), an organic manganese compound is currently added to petrol to replace tetraethyl lead as an antiknock fuel additive in the USA and

Canada; combustion exhaust gases contain manganese oxides. Lytle et al. (1995) show manganese oxides from motor vehicle exhaust contaminated plants close to roads; these manganese concentrations in soil and plants along roadsides often exceeded levels known to be toxic. Pirrone and Keeler (1996) estimate that emission of trace elements, such as manganese, from an iron-steel factory; waste incineration and non-ferrous metal production are steadily increasing. Mukherjee and Nuorteva (1994) detected toxic metals, including manganese, in the forest biota around an iron-steel factory in Raahe, Finland, determining the grade and extension of the metal deposition from bio-indicators. The content of heavy metals in rivers, close to urban areas, must also be considered in the preservation of historic monuments. Deely and Fergusson (1994), studied the maximum anthropogenic metal fluxes of an estuary and the necessary extra clean sediment needed to dilute the heavy metal content. Profiles rich in metal contents could be explained by historical events around the estuary and river, storm water drains and sewage plants. Increased metal concentration was found only in the lower reaches of the largest rivers and locally around known industrial pollution sources (Klavins et al., 2000). The preservation downtown Toledo is vital because of its historic heritage and the tourist revenue it attracts. The existence of a fully operational (1780-1985) steel mill (Real Fábrica de Armas de Toledo) on the north bank of the river Tagus and a steam power plant (Azeca, in Villaseca La Sagra) which spilled 25.000 liters of fuel-oil in the Tagus in the year 2000, as well as traffic pollution and central heating, has spread manganese into both waters and air of the Toledo's surroundings. It has also damaged Toledo's historic buildings as rainfall drops

this atmospheric pollution onto the ground, water, humans, animals, plants and buildings.

The formation and depositing of solid manganese oxides requires the oxidation from dissolved Mn^{2+} to Mn^{4+} . Experiments by King et al. (1999) on bioaccumulation studies of wastewater show oxidation occurring wastewater is biologically-mediated and linked to the particulate material or surfaces, e.g., manganese oxidising bacteria forming biofilms on the carapace of a crayfish, followed by MnO_2 precipitation. The deposition of brown-black manganese oxides on pipes, rocks and sediments, from overlying waters rich in manganese, have been widely documented (e.g., Tyler, 1970, Ehrlich, 1990, and Nealson, 1992).

Recently, Murdoch and Smith (1999) observed manganese micro-nodules within a biofilm growing on the surface of PVC and HDPE pipe and demonstrated the presence of the micro-nodules is dependent on the presence of manganese oxidising bacteria. They (Murdoch and Smith, 2000) concluded the levels of Mn^{2+} measured in the raw water decreased up to 100% after two month. The addition of *Pseudomonas* sp. to a culture increased the percentage of removal during the same period, the Mn^{2+} oxidation to Mn^{4+} to form MnO_2 micro-nodules can be a rapid process. Rough solid surfaces and carbonates help the manganese's precipitation from water, while the larger active surfaces of the clay brick also improve the manganese removal from water (Aziz and Smith, 1992).

The main purpose of this research was to determine probable sources and causes of manganese precipitation on a brick surface. Analyses by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were performed on pyrolusite micro-nodules to examine its morphologies, mineralogical and chemical composition and oxidation states of chemical elements. Additionally, these processes of manganese crystallization on the surfaces of bricks outlines an interesting industrial path for staining black surfaces and thus improving the external look of modern bricks, displaying an antique aspect.

2. Materials and methods

Samples of old bricks were collected from the upper part of an Islamic wall of gardens dated from the X Century, during the archaeological excavation at the Alcazar of Toledo (Fig. 1). The mineralised brick had been buried and withstood water solutions and high humidity environments. The surface show black dots of 0.1 mm in diameter that cannot be removed to be analysed. Because of this, analyses by SEM, XRD and XPS techniques were performed on this brick surface.

Waters from the El Torcón and Guajaráz reservoirs and Tagus River, which had possibly affected the bricks were analysed by inducted coupled plasma spectrometry and colorimetric techniques, as follows: iron and manganese by inducted coupled plasma; and aluminium, chlorine, ammonium, nitrates and nitrates colorimetric methods. The organic matter was determined by titration with potassium and oxalic permanganate in acid solution. For micro-organisms

(coliform and bacteria) the analysis method was membrane filtration. Additional routines such as average temperature, pH, conductivity, turbidity, organic matter, bacteria, algae was also carry out for these waters.

Textures and morphology of pyrolusite nodules were studied using optical and scanning electron microscopy (SEM). For this technique, brick surfaces were coated with gold (20 nm) in a Bio-Rad SC515 sputter coating unit. General SEM observations were carried out in a Philips XL20 SEM at accelerating voltages of 20-30 kV. Energy-dispersive X-ray microanalyses (EDX) were obtained using a Phillips EDAX PV9900 with a light element detector type ECON. The MnO_2 structural data and the brick mineralogy were determined by X-ray powder diffraction (XRD) using a Phillips powder diffractometer with $\text{CuK}\alpha$ radiation. Patterns were obtained by step scanning from 2° to 64° 2θ in steps of 0.020° with a count of 6 s per step.

X-ray photoelectron spectrometry (XPS) data were acquired with a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyser and a $\text{MgK}\alpha$ K-ray exciting source (1253.6 eV, $1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$). The samples were mounted on a sample rod placed in a pre-treatment chamber and heated at 423 K under vacuum for 1 h prior to being moved into the analysis chamber. The pressure in the ion-pumped analysis chamber was below 3×10^{-9} Torr ($1 \text{ Torr} = 133.3 \text{ N m}^{-2}$) during data acquisition. Twenty eV energy regions of the photoelectrons of interest were scanned at 20 eV spectrometer pass energy, chosen as a compromise enabling acceptable resolution to be obtained within reasonable data acquisition time. C1s , K2p , Ca2p , Fe2p y Mn2p peaks

were recorded. Intensities were estimated calculating the integral of each peak after subtraction of the S-shaped background and fitting the experimental curve to a mixture of Lorentzian and Gaussian lines of variable proportion. All binding energies (BE) were referenced to the adventitious C 1s line at 284.9 eV. This reference gave BE values accurate to within ± 0.1 eV.

3. Results and discussion

Images from scanning electron microscopy show manganese micro-nodules (ca. 2 μm in diameter) composed by micro-needles under a bio-film grown on the brick surface (Fig. 2). Fig. 2a shows the pyrolusite nodules between the brick surface and the bio-film bed. In many cases the pyrolusite nodules and semi-nodules are inlaid into the bio-film background showing several intermediate formation stages (Fig. 2b). Figure 2c shows fibrous aragonite formations characteristic of the underground spaces such as of karstic caves.

The X-ray diffraction of the brick background (powder) and brick surfaces display the following results (Fig 3): Minor amounts of illite (10.04Å) with several intermediate grades of crystallinity. This denotes different grades of bricks due to the highly irregular cooking temperatures of bricks by the Arab method (e.g., 24 hours firing a tip of raw bricks with wood and charcoal in a closed furnace). Large amounts of quartz (4.26 Å and 3.33Å peaks), which is a resistant phase during brick cooking and probably comes from the surrounding tertiary arkoses, themselves a weathering detritus of the Toledo migmatite facies. Mixed main X-diffraction lines of alkali and plagioclase feldspars (3.26-3.28Å peaks) that can be attributed to perthitic mixed samples characteristic of migmatite and gneiss

rocks. Variable amounts of calcite ($3.03\text{\AA}$ peak) from the natural raw material, and from the original mortar made with cooked chalk ($\text{CaO} + \text{H}_2\text{O} > \text{Ca}(\text{OH})_2$), secondary aragonite phases crystallizes from this raw carbonated materials. Hematite and goethite phases are not detected due to their low ratio in the sample which was below the detection threshold of the XRD, the use of X-ray copper tube and the rising of the background of the XRD profile (iron effect). Secondary calcium and magnesium silicate phases (gehlenite, wollastonite, diopside, etc.) from primary origin (i.e., baking reactions between calcium carbonate and aluminosilicates) and secondary formation also occasionally detected (i.e., hydraulic reactions of crystallization from amorphous reactive gels such as the cement case). Low XRD peaks of pyrolusite phase masked with other main phases. This analytical handicap stems from XRD diffraction analysis on the tiny black dots on the brick surfaces that prohibit the removal and concentration necessary for improved XRD profiles.

A survey X-ray photoelectron scan reveals the appearance of Al, Si, Ca, K, Fe, Mn and C elements. Selected energy regions of the most intense Al2p, Si2p, Ca2p, Fe2p, Mn2p and K2p+C1s emissions were then scanned a number of times, depending on peak intensity, to obtain good signal-to-noise ratios. The binding energies of the principal peaks are: K2p_{3/2} at 294.0 eV, and Si2p, Al2p and Ca2p_{3/2} at 102.8, 74.5 and 347.8 eV, respectively. The binding energy of the Mn2p_{3/2} peak at 642.2 eV confirms the presence of Mn^{4+} , which agrees with the pyrolusite MnO_2 phase. The Fe2p_{3/2} line profile results are complicated, not only by the appearance of a satellite structure but also for the broadening of the main peak. By applying peak fitting procedures two Fe^{3+} phases, attributed to

hematite Fe_2O_3 and goethite $\text{FeO}(\text{OH})$, are detected. Quantification of the elements gives the following surface atomic ratios, relative to silicon: $\text{Al/Si} = 0.452$, $\text{K/Si} = 0.067$, $\text{Ca/Si} = 0.525$, $\text{Fe/Si} = 0.078$, and $\text{Mn/Si} = 0.013$, indicating that Al, Si and Ca are abundant elements, with K, Fe and Mn as minor components. Different proportions of minerals on the analysed brick surface could explain this (alkali and plagioclase feldspars, quartz, illite, calcite, hematite, goethite, gehlenite and pyrolusite). In addition, the C1s line exhibits three components at binding energies 284.9, 286.8 and 289.5 eV, the two former account for C-C and C-O bond in organic matter, and the later is associated to CaCO_3 structures developed on the exposed Ca^{2+} ions on the surface particles of the brick (Fig. 4).

Recently, the water from the Torcón reservoir was considered undrinkable due to the presence of algae, bad organoleptic conditions (taste, aroma, texture, appearance) and manganese and ammonium concentrations exceeding the permitted limits. Traditionally, waters from the Torcón and Guajaraz reservoirs are treated with potassium permanganate and aluminium polychloride during the purification process. This additional source of manganese (Mn^{7+} in MnO_4K) cannot be disregarded in the speculations on the pyrolusite micro-nodules origin.

To obtain global information on Toledo's water, analytical data of the official COCA network checkpoints, from 1990 to 1998, were studied (see inset of Fig. 1 and Table 1): (point 3175) in the Jarama river and close to the Tagus junction. With 0,19 mg/l of manganese and heavy pollution from Madrid made this water,

unusable. This takes into account that a manganese concentration of 0.10 mg/litre is the Food and Agriculture Organization of The United Nations (FAO) recommended limit for irrigation (Spanish National Hydrological Planning, Sept. 2000); (point 3239) shows similar levels of 0.19 mg/l of manganese; (point 3014) has less Mn contents (0,11 mg/l) and more organic matter from Toledo's surroundings, (point 3151) in the Castrejon reservoir shows also 0,11 mg/l). The algae in the Torcón reservoir are *Oscillatorias agardhii* and *Microcystis aeruginosa* and *gomphosphaeria* in the Guajaraz reservoir. The analyses show 11,000 cellules/ml of algae in the Torcón reservoir. The pH value is approximately 7,3 in both reservoirs.

Airborne manganese from traffic, central heating or surrounding industries could be disregarded as possible sources of the pyrolusite micro-nodules because they are not accompanied by other typical airborne particles such as calcium sulphates (from SO₂ gas), black carbons or heavy metals (Pb, Cd, Ni). These manganese micro-nodules and bio-films on the old brick walls of the National Heritage Buildings of Toledo seem to have formed recently as a result of the waters from Toledo. The formation of the pyrolusite (MnO₂) nodules could be explained by the anthropogenic potassium permanganate in a reduction process ($\text{Mn}^{7+} > \text{Mn}^{4+}$) or by oxidation mechanisms from dissolved Mn²⁺ (from Mn²⁺ to Mn⁴⁺) linked to algae bio-film on the surface of this old brick.

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FIGURE CAPTIONS

Figure 1. Sketch map of the Toledo area, showing the points of water analyses, rivers and reservoirs.

Figure 2. Scanning electron microscope images of: (a) micro-nodules of pyrolusite onto brick surfaces. (b) detail of the close relationship between the MnO_2 nodules and the algae bio-film, (c) aragonite on the brick surface.

Figure 3. X-ray diffraction profile of a brick surface with black spots of pyrolusite.

Figure 4. Binding energies (eV) of core-electrons of the brick surface with black spots of pyrolusite: (a) Carbon, (b) Calcium, (c) Iron, (d) Manganese.

TABLES

Table 1. Average analytical data from Torcón, Guajaraz and Castrejón reservoirs, between 1987-2002.

FIGURE 1

Figure 2

Figure 3

FIGURE 4

Table 1

WATER	Castrejón (non treated)				Torcón and Guajaraz (non treated)	Torcón (treated)		
DATE	1987-1988	1989-1990	1991-1992	1993-1994	1995-1996	1997-1998	1999-2000	2001-2002
T (°C)	14,05	14,95	13,91	13,7	-	18,12	17,94	15,12
pH	7,6	7,01	7,05	7,4	7,56	7,29	7,48	7,34
Conduct. (µs/cm)	1229	1135	1259	1313	334	172,95	401,92	140,48
Turb. (ntu)	-	-	-	-	-	0,44	0,78	0,86
Cl- (mg/l)	107,4	101,2	131,7	147,4	36	0,51	0,51	0,48
NH4+ (mg/l)	7,59	5,93	7,8	9,63	-	0,091	0,095	0,098
NO2- (mg/l)	-	-	-	-	-	0,07	0,20	0,28
NO3- (mg/l)	9,18	8,3	10,01	11,18	2,4	3,10	3,17	2,03
Al3+ MgO2/l)	-	-	-	-	-	0,02	0,06	0,05
Fe2+ (mg/l)	$9,3 \times 10^{-2}$	8×10^{-2}	$8,6 \times 10^{-2}$	11×10^{-2}	0,1	2×10^{-3}	$4,2 \times 10^{-2}$	$3,35 \times 10^{-2}$
Mn2+ (mg/l)	$8,7 \times 10^{-2}$	$5,5 \times 10^{-2}$	$11,5 \times 10^{-2}$	0,1	2×10^{-2}	3×10^{-4}	4×10^{-3}	8×10^{-3}
Algae (cell/ml)	-	-	-	-	-	0	0	21,86
Organic matter (mg/l)	-	-	-	-	-	1,24	3,24	1,52