

THE FORMATION OF Pb(IV) OXIDES IN CHLORINATED WATER

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INTRODUCTION

Controlling plumbosolvency and lead release in drinking water distribution systems from lead pipes, brass fixtures, and lead-based solders is a goal of all water utilities. The U.S. Environmental Protection Agency's (USEPA) Lead and Copper Rule established an action level for lead at the consumer's tap of 0.015 mg/L in a 1 liter first draw sample (Federal Register, 1991a, 1991b, 1992). Since the Rule's passage, the understanding of relationships between water quality and the solubility of lead-containing minerals found in drinking water distribution systems has grown extensively. The impacts of factors such as pH, dissolved inorganic carbon (DIC), and orthophosphate on the solubility of Pb(II) solids are relatively well known (Schock & Gardels, 1983; Schock & Wagner, 1985; Schock et al., 1996; Schock & Clement, 1998), and when these factors are adjusted appropriately can be used to control lead levels at the tap.

While most water treatment and water chemistry specialists are very familiar with the radically different solubilities and scale formation properties of ferrous iron versus ferric iron, or cuprous copper versus cupric copper, there is much less realization of the same potential behavior of lead. Potential-pH diagrams for the lead system going back many years have a prominent stability field for the highly insoluble lead (IV) dioxide solid, PbO₂ (Delahay et al., 1951; Pourbaix et al., 1966; Schock, 1980, 1981; Schock & Wagner, 1985; Schock et al., 1996; Schock, 1999). Thus, an analogy can be drawn between the Pb(IV)-Pb(II) redox couple and the Fe(III)-Fe(II) redox couple. The higher oxidation state forms of the iron oxide or oxyhydroxide pipe scale phases have much lower solubility than those of the lower oxidation state. In the case of lead, however, the oxidation-reduction potential (ORP) required for the transformation of Pb(II) to Pb(IV) is much higher than for the ferrous to ferric iron transformation.

Several observations from lead pipe scale specimens from 34 different water systems have provided a reasonable hypothesis to explain the apparent anomaly observed in many field studies in which high alkalinity waters did not tend to produce nearly as high levels of lead release as would be expected from the knowledge of lead solubility chemistry and benchscale tests (Dodrill & Edwards, 1994; Dodrill, 1995; Dodrill & Edwards, 1995; Edwards et al., 1999).

Overall, the presence of PbO₂ is associated with waters of persistently high ORP, which are only possible by maintaining sufficient levels of free chlorine in waters in contact with lead service lines and other lead materials. Certain water chemistry conditions favor higher and persistent ORP. Some of these conditions include pristine low-NOM ground waters with little bulk oxidant demand allowing significant persistence of free chlorine; waters that effectively passivate iron and remove its oxidant demand (such as hard waters with high buffering intensity); waters with low oxidant demand resulting from oxidative treatments such as greensand filtration (enabling the stability of high ORP); and many other possible scenarios. An additional example of waters

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with a high ORP are those that contain a high concentration of free chlorine to combat biofilm problems or to overcome corrosivity towards iron and its pipe wall demand.

The pipe scale analysis observations have raised a number of important questions: How prevalent is Pb(IV) in drinking water distribution systems? Can it occur in some parts of a water distribution system, and not others? What is the significance of the presence of Pb(IV) relative to lead release, and how does it impact lead treatment guidance? How quickly and by what pathways are Pb(IV) solids formed, and how stable are they in response to a variety of water treatment changes? What is the chemical pathway by which PbO₂ solids are broken down, and why does it cause periodic increases in lead levels? In addition, these observations draw attention to a large gap in the thermochemical data in terms of the solubility and speciation of tetravalent lead for these minerals, making difficult to precisely and accurately model either (Schock, , 2001; Schock & Giani, 2004).

Because of the many questions surrounding the occurrence of tetravalent lead solids and their relationships to lead release, this research investigation was initiated in 2002 in order to (1) explore the water quality conditions and pathways that lead to the formation of PbO₂ in water during long term precipitation experiments and to (2) determine the possible sensitivity of PbO₂ scales to treatment changes that would affect ORP by analyzing the stability of the solids in response to changes in ORP. The physical properties, mineralogy, and solubility of lead solids at several pH values in well chlorinated water were examined, and the effect of sulfate on PbO₂ formation was also briefly investigated.

Pb(IV) LITERATURE BACKGROUND

Lead dioxide, PbO₂ has two polymorphs: plattnerite (β -PbO₂) and scrutinyite (α -PbO₂). Plattnerite is the tetragonal dimorph of lead dioxide and in mineral form is brownish black to black in color with a dark red streak. Scrutinyite is orthorhombic in structure and dark reddish brown in color (Greninger et al., 1975). The name alludes to the close scrutiny that is necessary to distinguish it from plattnerite. Greninger et al. (1975) also observed that PbO₂ solids may readily function as semiconductors. Thus, there is likely to be considerable electrochemical reversibility and ease of electron transport between the water and the underlying lead metal of the pipe. Changes in the scale makeup in responses to ORP are rather fast and measurable.

The bulk of the literature on PbO₂ is associated with the battery industry. Some of the key conclusions from the literature are summarized as follows:

- The deposition of scrutinyite (α -PbO₂) occurs in both basic and acidic solutions at low current densities while plattnerite (β -PbO₂) can only be obtained in acidic media at high current densities (Hampson, 1979)
- The cyclic corrosion process taking place at the lead/lead dioxide interface was controlled by an inner corrosion product layer of α -PbO₂ and an outer layer of β -PbO₂ (Velinchenko et al., 1995)
- Certain perchlorate salts have an effect on formed PbO₂, particularly on its discharge properties, self discharge, and its active surface area (Pettersson, Ahlberg and Berghult, 1998)
- PbO₂ structure and morphology exerts an influence on its electrochemical activity (Pavlov et al., 2004)
- H₃PO₄ increases the ratio of α - to β -PbO₂ of corrosion scales (Bode & Voss, 1962; Tudor et al., 1967)

The oxidation-reduction potential where PbO₂ becomes stable is at very high potentials starting near the upper stability boundary for water (Figure 1, page 8). The high redox potential

necessary to achieve PbO₂ formation in water can only be met with the use of strong oxidants (e.g., free chlorine, chlorine dioxide, etc.) and their persistence into the distribution system.

MATERIALS AND METHODS

A series of long-term precipitation experiments were conducted to evaluate the effects of water chemistry and time on the mineralogy and corresponding solubilities of lead solids in water. During these tests, redox conditions were chosen to represent the high end of realistic utility practices and were maintained with the intent to form Pb(IV) solids (plattnerite and/or scrutinyite). High redox potential of the water was maintained with free chlorine, which was replenished as needed to maintain a goal concentration of 3 mg Cl₂/L throughout most of the studies. Late into the test runs, chlorine residuals were permitted to dissipate to test the reversibility of mineral phase development. One run was performed in water containing sulfate to investigate the role of an additional major anion on the development of lead solids. Lead (II) sulfate and hydroxyl-carbonate-sulfate solids have been observed in some lead drinking water pipes. All experiments were conducted at room temperature (~23 °C).

Lead aging studies were conducted in a 3.0 liter glass beaker. Secured at the top of the beaker were pH and two redox electrodes, dissolved oxygen (DO) and temperature probes, a mechanical stirrer and an injection line for both acid and base. The computer software recorded pH values and titrant volumes. Data was collected on the pH, dissolved oxygen, redox potential, free and total chlorine, and concentrations of lead, sulfur and total inorganic carbon. In addition the crystalline phases of lead solids were identified using X-ray diffraction (XRD).

RESULTS

A summary of the lead precipitation test runs conducted in this study is provided in Table 1 on page 14. Typically, these runs lasted more than 240 days and were conducted at three initial pH values: 6.5, 8, and 10. However, because no attempt was made to maintain constant pH levels during each test run, the final pH values varied to some degree from the initial values. The authors recognize the control of pH and ORP during the experiments was limited, and the following results should be interpreted accordingly. Given the difficulty and sensitivity of the experiments, and time necessary to achieve anticipated results, the ability to maintain initial water quality conditions was nearly impossible. Nonetheless, the findings do at a minimum demonstrate conditions and pathways which Pb(IV) oxides do form in water, and corresponding lead solubility changes.

Experiment A. Experiment A was conducted initially at pH 8 in water with a dissolved inorganic concentration (DIC) of 10 mg C/L. During this run, the final pH was relatively consistent (pH 7.75 to 8.19) throughout the entire 397 day test period. Free chlorine was adjusted on day 26 and 105 to maintain the redox potential of the water and to regain lost chlorine. Chlorine was completely consumed during the days prior to these readjustments. Because no effort was made to maintain chlorine residual beyond 105 days, chlorine levels were completely depleted sometime between days 105 and 395. The remaining sample at the end of the study had consumed nearly 9 mg Cl₂/L. The redox potential of the water was approximately 942 mV (vs. SHE) when the maximum free chlorine dose of 3 mg/L was achieved and was approximately 440 mV (vs. SHE) at the end of the study when no chlorine was present.

The color of the lead precipitate visible in the water sample bottles changed gradually but dramatically from white to dark orange-red color over the first 82 days of the study (Figure 2, page 9). The dark red color somewhat resembled the recognizable color of iron (III) precipitates and corrosion deposits. The red solid gradually disappeared (Figure 2 – 145 and 397 days) as chlorine was consumed to the eventual point of depletion. At the completion of the study, only white lead

solids were filtered from the water and no visible red color was observed. This establishes that lead particle transformations are both reversible and redox dependent.

XRD analysis of the filtered solids showed the dynamic nature of lead mineralogy over the aging period (Figure 3, page 10). During the first 7 days, hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, was the dominant lead phase present and a trace amount of cerussite, PbCO_3 , was also detected. On day 18, the major solid phase shifted to cerussite and only a trace amount of hydrocerussite was detected. By day 64, neither cerussite nor hydrocerussite were present, but plattnerite ($\beta\text{-PbO}_2$) was detected, along with a small amount of scrutinyite. Plattnerite and scrutinyite are Pb(IV) lead oxide polymorphs believed to be responsible for the red color of the lead particles (Figure 2, page 9). Plattnerite is reported as brownish-black to black with a red-brown streak, and scrutinyite, a dark reddish brown color. However, color is affected by crystal size, impurities, and other factors. The day 82 XRD scan was plotted against the pattern of a plattnerite standard (Figure 4, page 11) to provide an additional reference and evidence for the presence of PbO_2 . Interestingly, although the two XRD patterns are identical, the plattnerite standard was black in color and the dominant color of the experimentally precipitated lead was dark red. After 82 days, the XRD pattern scan was still dominated by plattnerite and scrutinyite. The presence of scrutinyite became more prominent with time, suggesting that it may be an aging product of PbO_2 and the more thermodynamically stable phase. Once again, there was no evidence for the presence of hydrocerussite. On day 145, plattnerite and some scrutinyite continued to dominate the mineralogical composition of the lead solids, and a trace of cerussite reappeared at this time. This observation coincided with the color changes and suggests that the formation of PbO_2 is reversible. At the end of the study (day 395), cerussite was the only lead solid mineral identified. The XRD pattern of cerussite at this time was sharper and more complete (based on the number of pattern lines) than the patterns identified earlier. Additionally, all traces of PbO_2 phases were gone. Soluble lead levels (based on a $0.2 \mu\text{m}$ filter) throughout this aging test run showed a dramatic change in lead solubility (Figure 5, 12) corresponding directly to the change in lead solid color and mineralogy.

Experiment B. Experiment B was conducted at an initial pH of 6.65 in water having a DIC of 10 mg C/L. The pH of the water during the run was not as consistent as the pH during Experiment A, increasing to as high as 7.56 over the aging period. No chlorine adjustment was made through the first 140 days. Consequently, free chlorine levels dropped from 3 mg/L down to only 1.4 mg/L during the testing period. At the initial pH and chlorine concentration, the redox potential was 1099 mV (vs. SHE). Like Experiment A, the color of the precipitated lead visible in the sample bottles changed with time. The lead solids turned from white to dark red; these changes became particularly apparent by day 63. The red color of the solids appeared to be nearly identical to the solids that formed in Experiment A.

Stereomicrograph images of lead particles were collected as they were trapped on the filter at various times throughout the study. Although the particles were similar in appearance to those collected during Experiment A, these particles (especially the particles darker in color) were sparse and distinct. XRD results showed that the lead minerals transformed with time from a mixture of cerussite and hydrocerussite (first day of experiment) to cerussite alone (days 4 and 14), and then back to a mixture of cerussite and hydrocerussite on days 21 and 33. By day 62, plattnerite was present along with cerussite and a trace amount of scrutinyite. This mixture of solids was present in all runs until the end of the experiment (97 days). The prevalence of both PbO_2 phases appeared to increase with time, based on relative changes in XRD pattern intensities.

Experiment C. Experiment C was conducted to evaluate the impact of sulfate (210-218 mg SO_4/L) on the aging of lead solids at pH 8 (7.75 to 8.0) and 10 mg C/L. Free chlorine was not adjusted during the entire study period. At ninety-three days into the study, nearly 1 mg Cl_2/L was still measured and by the end of the study no free chlorine was present. The initial redox potential

was 967 mV (vs. SHE) and dropped to 492 mV (vs. SHE) by the end of the test run. Again, like in previous experiments, the color of the precipitated lead turned from white to dark red.

As in Experiment A, a mixture of small, distinct, dark red particles sat on a background of lighter red-colored solids. At 71 days, there were a large number of large, dark-colored particles present. XRD results showed that initially (day 0), hydrocerussite was the only solid identified. Cerussite joined hydrocerussite as the only lead materials present by day 7. Hydrocerussite disappeared by day 14 and cerussite was the primary solid identified. Traces of plattnerite and scrutinyite were also detected. After this time, cerussite continued to be the dominant solid present for the remainder of the study. The presence of plattnerite and scrutinyite grew with time and were also present through the remaining study period. Day 70 showed the strongest pattern for plattnerite, which also corresponded with the large number of dark particles observed simultaneously.

Experiment D. Lead aging Experiment D was conducted at an initial pH of 10 (9.72 to 9.86, DIC= 10 mg C/L, 23°C). Chlorine dropped rapidly during this test run and had to be replenished after only 29 days. The initial redox potential when free chlorine was 3 mg/L was 742 mV (vs. SHE). Sample color changed from white to light brownish-red after only 7 days. This color continued to become increasingly darker until day 30. Figure 6 (page 13) compares the color of filtered lead solids at pH 8 (Experiment A) and pH 10 (Experiment D). The lead particles formed at pH 10 have a stronger brownish tint than those formed at pH 8. Stereomicrographs of magnified lead particles, aging from 0 to 19 days, showed an increased presence of small, dark red particles (not shown). Initial XRD diffraction analysis showed the presence of only hydrocerussite. However, by day 7 plattnerite and scrutinyite joined hydrocerussite. After 19 days, plattnerite disappeared leaving only scrutinyite and hydrocerussite in the pattern. Finally, after 29 days when hydrocerussite was no longer apparent, scrutinyite was the only identifiable lead mineral phase remaining.

CONCLUSIONS

The results revealed that the Pb (IV) oxides plattnerite and scrutinyite (PbO_2) will form with time in chlorinated ($< 3 \text{ mg Cl}_2/\text{L}$) water at pH 6.65 to 10. These findings have raised a number of potential practical implications. The most concerning is the redox control on lead mineralogy and its corresponding solubility. Distribution systems that have historically maintained high chlorine residuals could have PbO_2 functioning to limit lead release, while they are presuming hydrocerussite or cerussite to be the main components of the passivating films or other diffusion barriers. As noted previously, the relative ease with which PbO_2 can form at neutral pH in waters with persistent free chlorine residuals suggests that PbO_2 likely occurs in many systems with substantial lead piping and where lead levels are unusually low relative to what would be expected for the divalent lead carbonate or hydroxycarbonate solubility at the ambient pH and alkalinity. Changes in pH, drops in ORP, or both could destabilize these PbO_2 films, and thus increase plumbosolvency and possibly increase the release of scale particles (Schock & Giani, 2004; Edwards & Dudi, 2004). Observations that have been made by some water systems of erratic lead release from lead service lines, and increases or decreases without clear correlations with pH, DIC, and temperature, may be caused at least in part by effects of ORP changes. Water systems may have a false sense of security about the successfulness of their corrosion control strategy due to the lack of observation and understanding of the pipe deposit mineralogy.

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Any opinions expressed in this paper are those of the author(s) and do not, necessarily, reflect the official positions and policies of the USEPA. Any mention of products or trade names does not constitute recommendation for use by the USEPA.

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FIGURES & TABLES

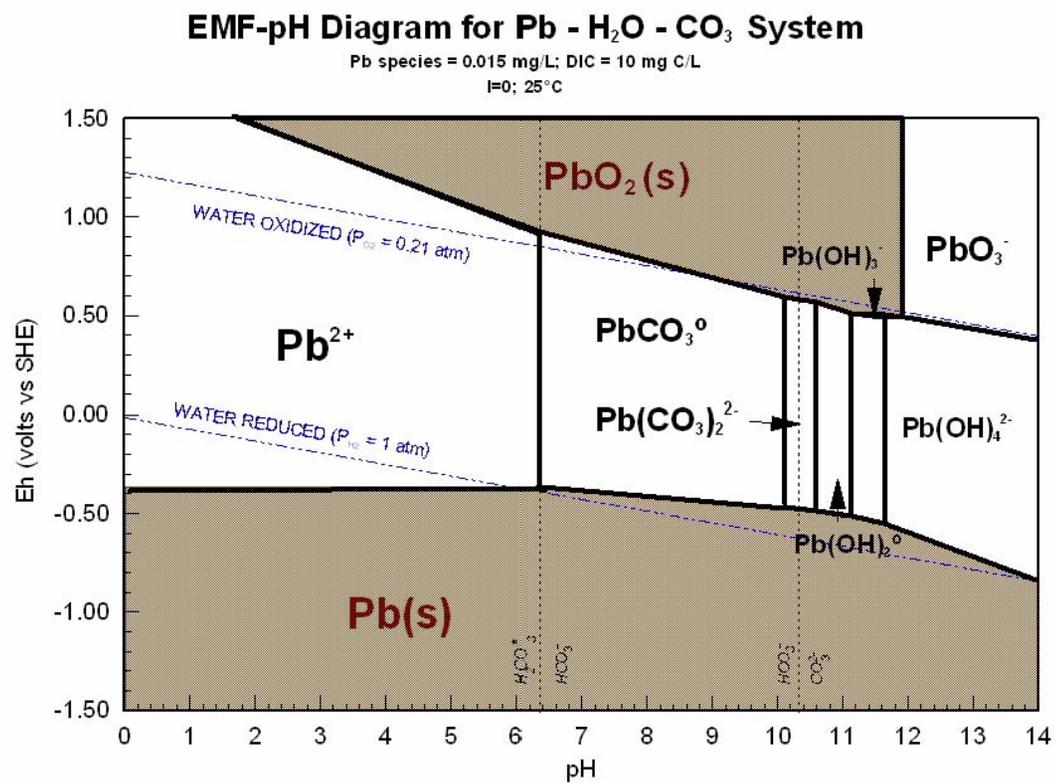


FIGURE 1. Eh-pH diagram for Pb-H₂O-CO₃ system (0.015 mg Pb/L, 10 mg C/L DIC, I=0, and 25°C).

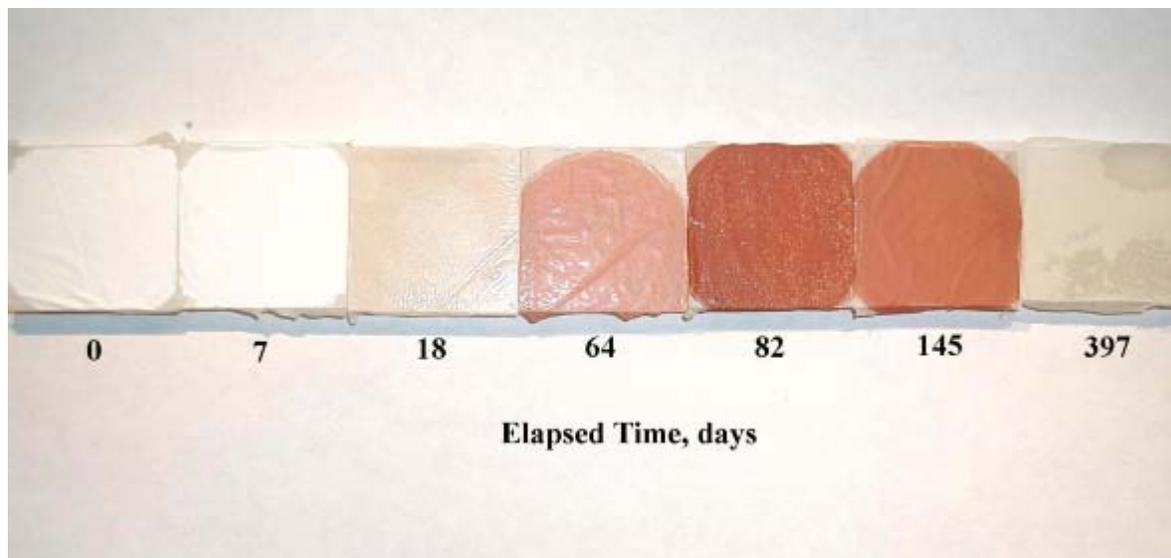


FIGURE 2. Color transformation of lead solids during Experiment A (DIC = 10 mg C/L, 24°C, pH 7.75 - 8.19).

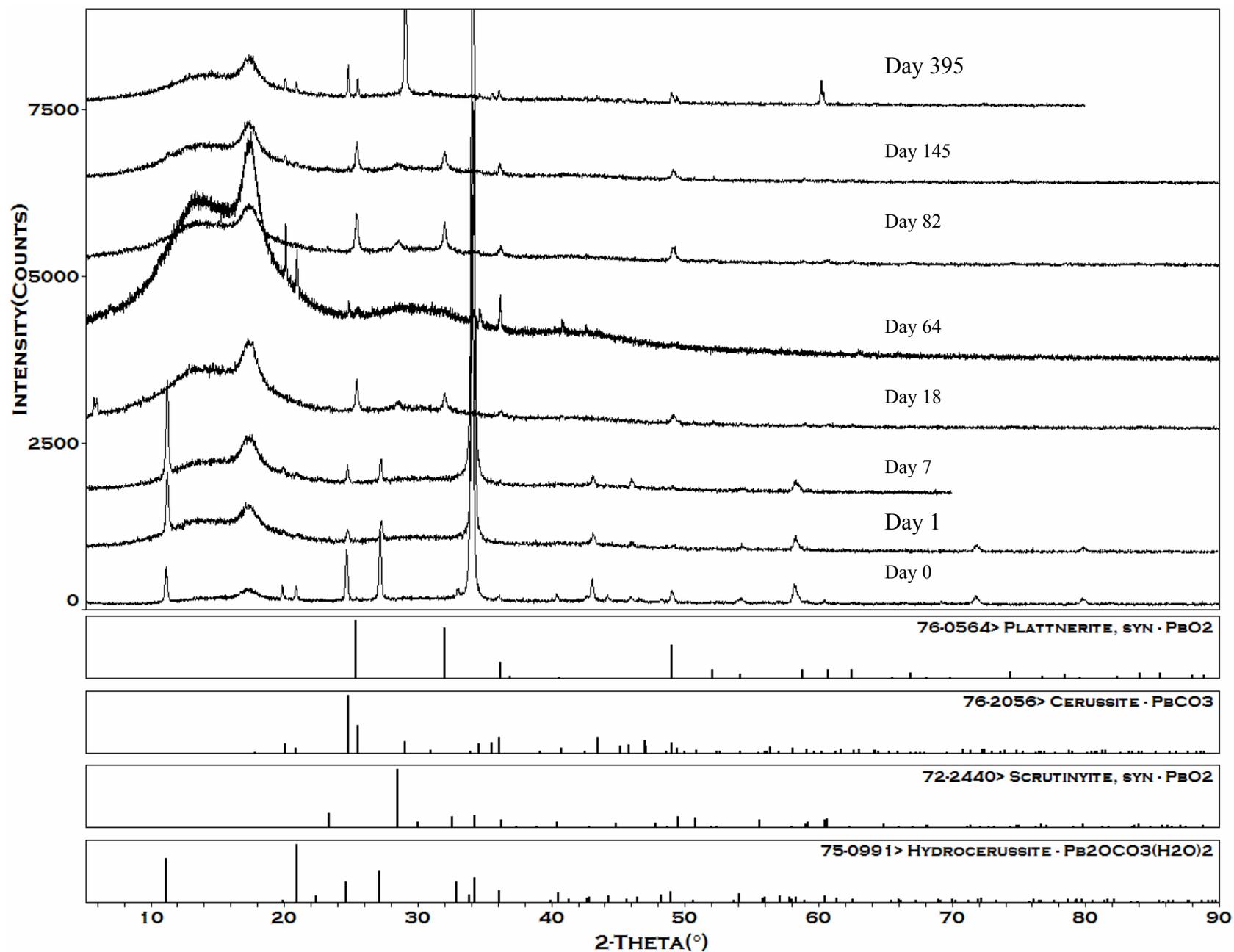


FIGURE 3. X-ray diffractogram of lead solids during experiment A (DIC = 10 mg C/L, 24°C, pH 7.74 - 8.19).

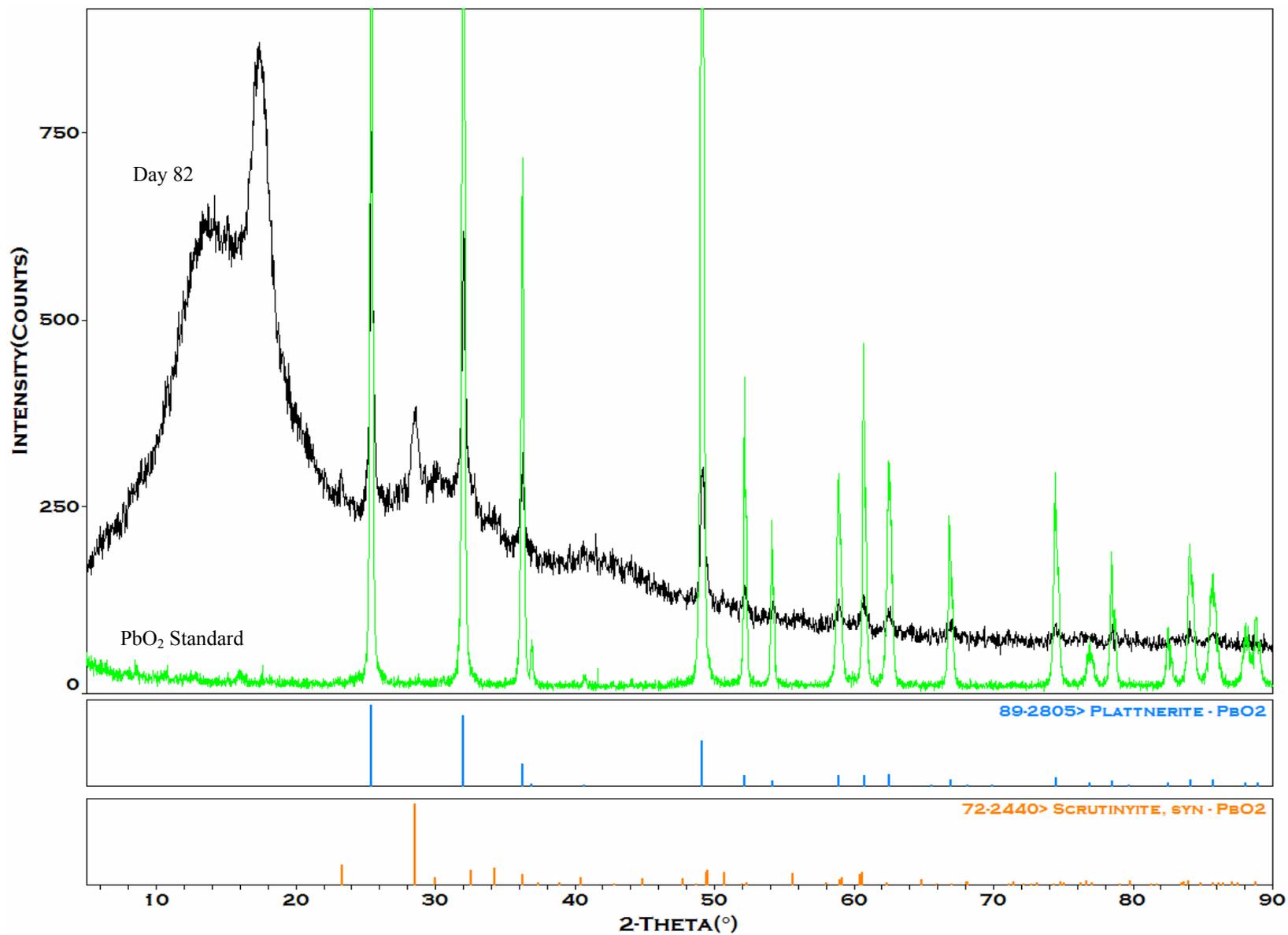


FIGURE 4. X-ray diffractogram of PbO₂ collected in Experiment A compared to a plattnerite PbO₂ standard.

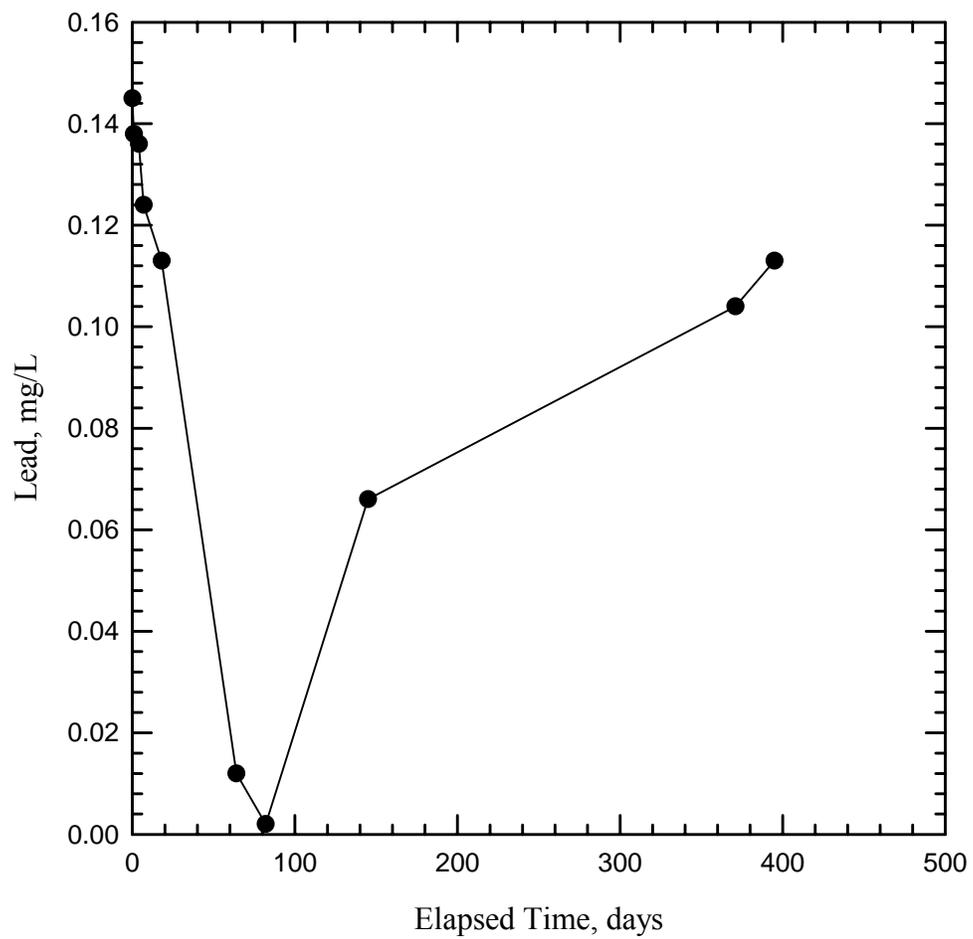


FIGURE 5. Soluble lead measured over time during experiment A (DIC=10 mg C/L, 24°C, pH 7.75-8.19).

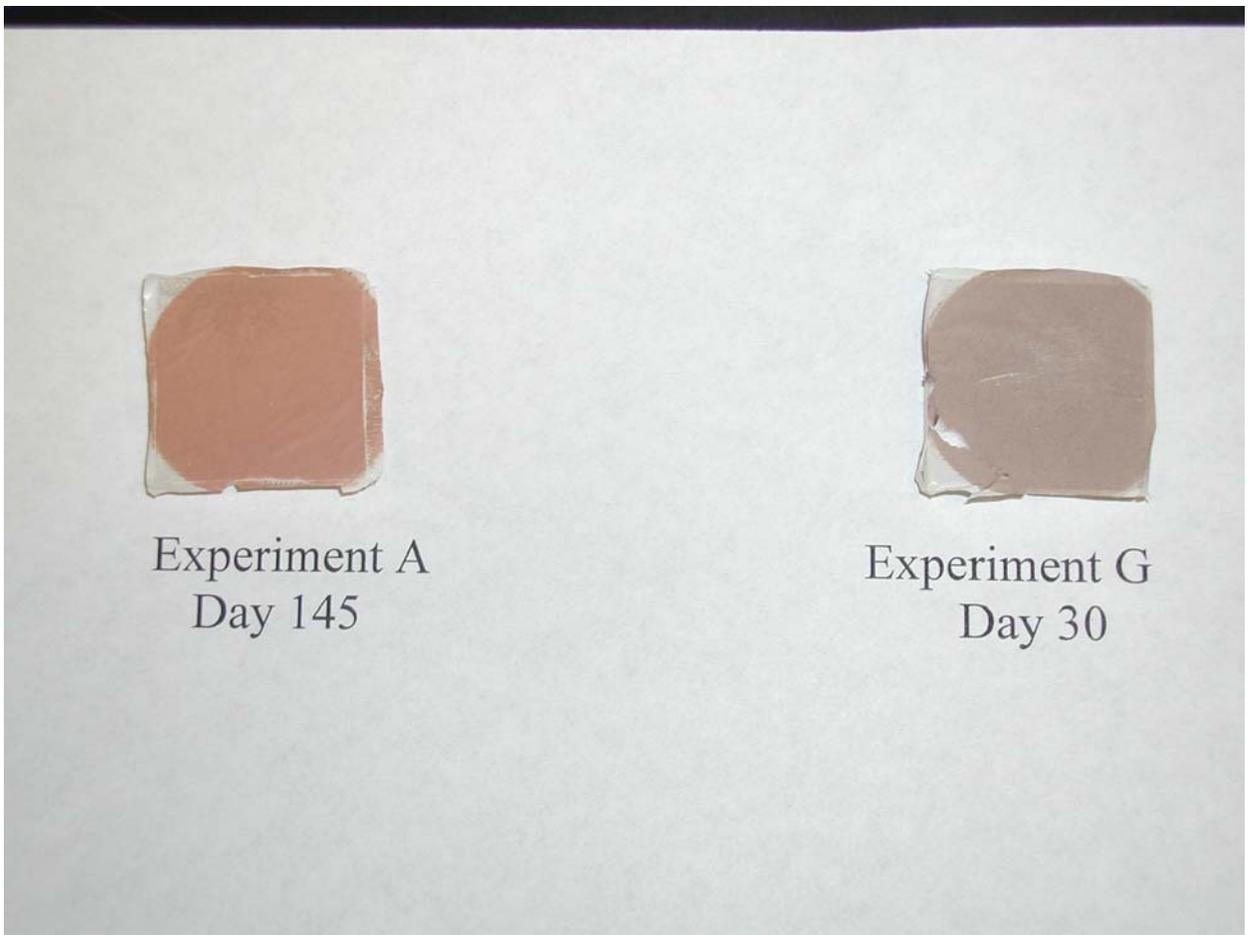


FIGURE 6. Color differences in lead solids produced at pH 8 (Experiment A) and pH 10 (Experiment G).

TABLE 1. Summary of experimental conditions.

Study ID	Elapsed Time, days	pH	Free Chlorine, mg/L	Measured Redox Potential, mV	Chlorine Adjustment on Elapsed Days
Study A	397	7.75-8.19	0.1-3.0	707-201	26,105
Study C	329	6.6-7.81	0.1-2.9	850-202	none
Study D	310	7.71-8.6	0.1-3.0	725-225	none
Study G	30	9.62-9.86	0.8-3.0	500-200	20