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# Durability of concrete containing siderite-bearing microsyenite and trachyte aggregates

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**Abstract**

The durability of concrete containing siderite-bearing microsyenite/trachyte aggregates has been investigated. The aggregates were from a disused Mt Gibraltar quarry and the Nattai River Cut 5 in the Bowral/Mittagong districts, 100 km south-west of Sydney in New South Wales, Australia. Laboratory and field exposures of embedded rock discs in mortar, and concrete and rock samples, conducted under controlled and measured environmental conditions, have shown the alteration of siderite secondary mineral in the Mt Gibraltar rock to iron oxides/hydroxides through oxidation processes. The rate of such alteration was generally found to be slow to moderate, but it was more profound in an alkaline environment. These findings are consistent with the theoretical desktop study of Eh–pH diagrams. Although the in situ oxidation of the siderite was visually observable, as pinhole-sized rust spots, the mobility of the iron and subsequent staining on concrete surfaces was negligible. The field inspection and subsequent petrographic study of existing concrete structures, made from siderite-bearing microsyenite/trachyte aggregates, have shown some degrees of in situ oxidation of the siderite to iron oxides/hydroxides, but no associated iron staining on concrete surfaces. No visual defects were observed in concrete structures in service for up to 80 years. Furthermore, it has been shown that the accelerated weathering techniques, developed in this study, can be used in future assessments of quarried rock during the various phases of any investigation.

*Keywords:* Concrete; Concrete durability; Aggregate; Siderite; Microsyenite; Trachyte; Secondary minerals

## 1. Introduction

Opinions are divided about the suitability of using siderite-bearing microsyenites or trachytes as a hard rock source for aggregates in concrete production. In the Bowral/Mittagong district, 100 km south-west of Sydney in New South Wales, Australia, there are several early to middle Jurassic microsyenite igneous intrusions that have been used in concrete production in the past, or are currently being assessed as a potential aggregate source. The main cause for concern, which has led to conflicting views on the potential long-term performance of this rock, is the presence of the secondary mineral siderite ($FeCO_3$). Previous studies [1–4] have indicated that siderite has the potential to oxidize under atmospheric conditions to iron oxides/hydroxides. This has led to concerns that siderite present in the aggregate of a concrete can oxidize and cause unsightly iron stains on the surface of the concrete, and/or the development of weaknesses in bond strength at the paste-aggregate interface. In the Bowral/Mittagong district, the mineral represents on average 5–15% of the rock; it is often found replacing (through deuteric alteration) the pyroxene in the rock. As the occurrence of siderite associated with any igneous deposit is rare, reference to its effect on durability of concrete in the literature is non-existent.

The rocks used in this study were sourced from a disused quarry at Mt Gibraltar near Bowral, and the Nattai River Cut 5 located on the Mittagong Bypass. The Mt Gibraltar rock was a typical microsyenite from the region (except for the presence of accessory chalcedony), while the rock sourced from the Nattai River Cut 5 was much finer

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grained and displayed a trachytic texture. Both rocks contained siderite (10–11% by modal volume) as a secondary mineral phase replacing pyroxene.

In this study, four existing structures that have been in service from 9 to 80 years were examined visually and also petrographically to establish if there was any adverse staining and/or structural deficiencies. These structures were prepared with siderite-bearing microsyenite aggregate from Mt Gibraltar, and trachyte aggregate from the Nattai River Cut 5. Also, concrete (Mt Gibraltar rock as aggregate) and mortar samples (embedded Mt Gibraltar rock slices) were exposed in Sydney for three years to establish if the oxidation of siderite would lead to any staining. In addition, polished rock samples, and embedded rock discs in mortar and concrete slabs were subjected to accelerated exposures in a laboratory study. Subsequently, petrographic studies were carried out to establish whether siderite, as a secondary mineral in dense microsyenites and trachytes, would lead to any staining or cause any changes to the aggregate transition zone (cement–aggregate interface).

The stability of siderite in a concrete environment depends on the basicity (pH), oxidation potential (Eh) and total dissolved carbon, iron and sulphur in the pore water of the concrete. Thus, a theoretical study was also conducted to examine the effect of basicity and oxidation potential on the conversion of siderite to iron oxides/hydroxides.

## 2. Experimental procedure

### 2.1. Accelerated exposures in laboratory

To evaluate the potential for iron staining in concrete prepared from siderite-bearing aggregates, four types of specimens were tested in a range of accelerated exposures. Microsyenite rock samples were collected from a disused quarry at Mt Gibraltar, and Kulnura coarse aggregate was chosen for a control concrete. General-purpose (GP) cement was used with Nepean River coarse sand and a fine sand from the Penrith Lake Development Scheme. The following specimens were prepared:

- Mt Gibraltar polished thin rock sections (76 × 50 mm), 30 μm thick, for transmitted light petrographic study.
- Mt Gibraltar polished rock slices (76 × 50 × 10 mm), for reflected light petrographic study.
- Embedded rock discs in mortar (referred to as mortar slab), consisting of diamond-cut thin circular Mt Gibraltar rock discs of 50 mm diameter and 3 mm thick in 150 × 300 mm mortar slab 20 mm thick. The discs were embedded in such a way that each circular surface lay approximately 2–4 mm from the exposed surface of the mortar slab. The mortar has a water to cement ratio of 0.55 and a cement:coarse:fine sand ratio of 1.47:2:1. These slabs were wet cured for three days prior to exposure in standard laboratory conditions until the time of exposure.
- Concrete slabs of 20 × 300 × 300 mm were cast from laboratory-crushed Mt Gibraltar aggregate or a commercial Kulnura aggregate. Table 1 shows the mix proportions of the concrete mixtures for the preparation of the concrete slabs.

Table 1
Mix proportions of nominal grade 32 concrete mix (kg/m$^3$)

| Mix constituents | Kulnura (control) | Mt Gibraltar |
|---|---|---|
| GP cement | 300 | 320 |
| 20 mm aggregate | 585 | 575 |
| 10 mm aggregate | 585 | 570 |
| Coarse sand | 645 | 635 |
| Fine sand | 70 | 70 |
| Water | 165 | 190 |
| Water-reducing admixture | 1.86 | 1.85 |
| Superplasticizer | 1.69 | 6.00 |
| Water/binder | 0.56 | 0.60 |

It should be noted that Kulnura aggregate was used for the casting of the control concrete slabs only, and no rock slice nor thin section were tested as this rock contains no siderite. The specimens were subjected to the following exposure regimes.

#### 2.1.1. Accelerated UV and IR radiation cycles

The weatherometer was programmed so that specimens were subjected to repeated 140 min cycles, consisting of 120 min (UV and IR) radiation with no water sprays, followed by 20 min of light water spray with UV radiation. During the radiation period, the temperature of the specimens was approximately 65 °C, falling to 23 °C during the water spray period. The concrete, mortar and rock slices were examined after various periods up to 385 days (3958 cycles) exposure, while thin sections were examined petrographically up to 319 days (3279 cycles).

#### 2.1.2. Water wetting and drying cycles

A circulating tank system was set up in a 38 °C controlled room that allowed automatic wet and dry cycling of specimens (2 cycles a day of 1.5 h wet/10.5 h dry). The concrete, mortar and rock slices were examined after various periods of exposure up to 385 days (3958 cycles) exposure, while thin sections were examined petrographically after various periods of exposure up to 319 days (3279 cycles).

#### 2.1.3. Salt wetting and drying cycles

A circulating tank system was set up in a 38 °C controlled room that allowed automatic wet and dry cycling of specimens (2 cycles a day of 1.5 h wet/10.5 h dry) using 3% NaCl salt solution. Polished rock slices were photographed after 154 days (308 cycles) exposure, concrete and mortar slabs after 154 days (308 cycles) and 256 days (512 cycles), while thin sections were examined petrographically after 91 days (182 cycles) and 190 days (380 cycles).

#### 2.1.4. Immersion in alkaline solution

A number of rock slices and thin sections were sealed tight in plastic containers at 38 °C containing an average artificial pore solution, i.e. a supersaturated solution of $Ca(OH)_2$ containing 0.08 mol/L Na and 0.15 mol/L K. Polished rock slices were examined after 154 days and 256 days immersion, while thin sections were petrographically examined after 91 days of immersion.

### 2.2. Outdoor exposures

In addition to the accelerated exposures, concrete and mortar slabs were exposed at an outdoor exposure site at CSIRO's North Ryde laboratories in Sydney (inland), which were examined visually for three years.

### 2.3. Inspection of existing structures

Visual examinations of three structures and one demolished structure in the Bowral/Mittagong district were carried out to establish whether the siderite in the aggregate has led to any iron stains on the concrete surfaces and/or any structural deficiencies. The structures were: a water tank (ca 1900) and the Austral office building (ca 1930) in Bowral, and a continuously reinforced concrete pavement (CRCP) and a demolished bridge (both constructed in the 1990s) in the Mittagong Bypass (Hume Highway). The concrete in the water tank and in the Austral office building was prepared from aggregates from Mt Gibraltar, whereas the concrete used in the CRCP and the bridge was reported to be made with aggregates from Nattai River Cut 5.

In addition to the visual examinations, detailed petrographic studies were carried out on an old concrete curb sample collected from the disused quarry at Mt Gibralter (about 80 years old), and concrete samples collected from a demolished bridge in the Mittagong Bypass.

### 2.4. Theoretical stability of iron compounds

The influence of the basicity and the oxidation potential on the stability of siderite was studied. The effect of dissolved carbon on the pore water of the concrete on the stability of siderite was also studied.

## 3. Results

### 3.1. Specimens subjected to accelerated exposures in laboratory

Following are the observations made on polished thin sections, polished rock slices, and mortar and concrete slabs subjected to the accelerated exposures in laboratory.

#### 3.1.1. Accelerated UV and IR radiation cycles

The visible change in appearance of the concrete and mortar slabs after exposure was negligible, although all the exposed surfaces tended to become darker (pinkish-

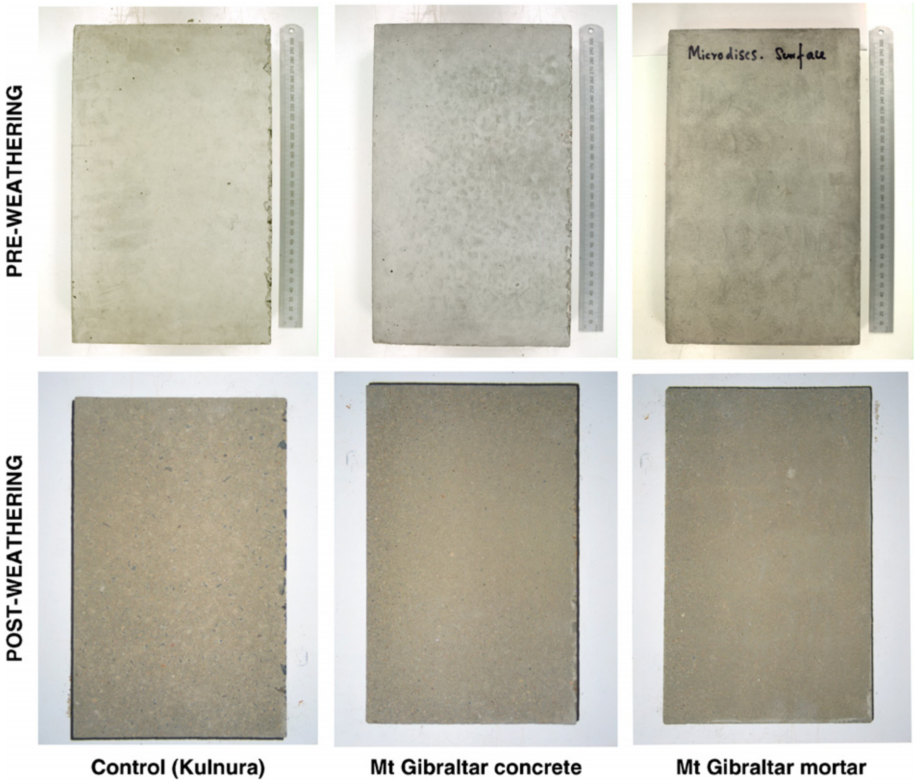


Fig. 1. Surface appearance of specimens pre-weathering and after 385 days (3958 cycles) in the weatherometer.

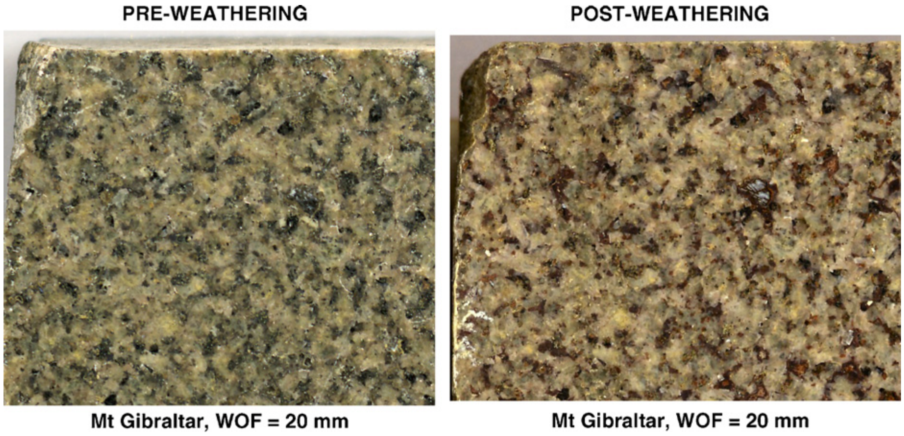


Fig. 2. Surface appearance of polished rock slice pre-weathering and after 385 days (3958 cycles) in the weatherometer.

green), porous and friable. There was no evidence of any rust spots (Fig. 1). The polished rock slices showed pinhole-sized rust spots and had distinctly changed in color from gray to pinkish-gray (Fig. 2). It was also worth noting that the rock slices, which had been kept at 23 °C and 50% RH in a lighted room, had also tended to turn to a pinkish-gray color. In thin section, the alteration of the siderite was quite variable. After 190 days exposure, all thin section samples showed some limited degree of alteration to iron oxides/hydroxides (Fig. 3), while they were more extensively altered after 319 days exposure.

### 3.1.2. Water wetting and drying cycles

Apart from some water stains (due to uneven drying), the visible change in appearance of the concrete and mortar slabs after cycling was negligible. After 319 days exposure, all rock slices showed loss of polish, while the Mt Gibraltar specimen had a distinct change in color from gray to pinkish-gray. In thin section, the alteration of the siderite was quite variable, with some tendency for minor iron staining along cracks and cleavage planes, or general cloudiness.

### 3.1.3. Salt wetting and drying cycles

Concrete and mortar samples in the saltwater tank displayed no visible staining due to the decomposition of siderite. The surface of the concrete and mortar slabs showed degradation (fretting) due to salt attack and water staining and, as a result, some of the coarse aggregate in the concrete slabs had been exposed.

In the second saltwater tank, the polished surface of some rock slices had been significantly degraded leaving a pitted (semi-polished) flat surface – due to the plucking out of clay minerals. The polished rock slices also showed pinhole-sized rust spots. The alteration of the siderite in thin section was slow and appeared internally as minor iron staining along cracks and some cleavage planes, or as general cloudiness.

### 3.1.4. Immersion in alkaline solution

Only rock slices and thin sections were immersed in alkaline solution. After immersion, apart from a general darkening of the surface and an occasional pinhole-sized rust spot, there was very little change to the polished surface of the rock slices. In contrast, the siderite minerals observed in thin section exhibited extensive alteration to iron oxides/hydroxides after only 91 days immersion (Fig. 4).

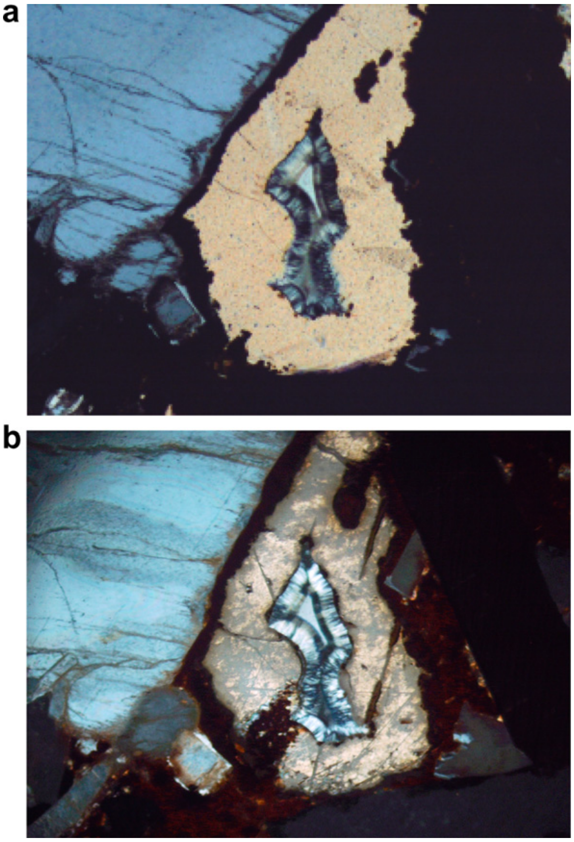


Fig. 3. (a) Siderite (vein) in thin section showing minor alteration, pre-exposure to weatherometer, WOF = 1.75 mm, XPL. (b) Siderite in thin section showing limited degree of alteration after 190 days exposure to the weatherometer, WOF = 1.75 mm, XPL.

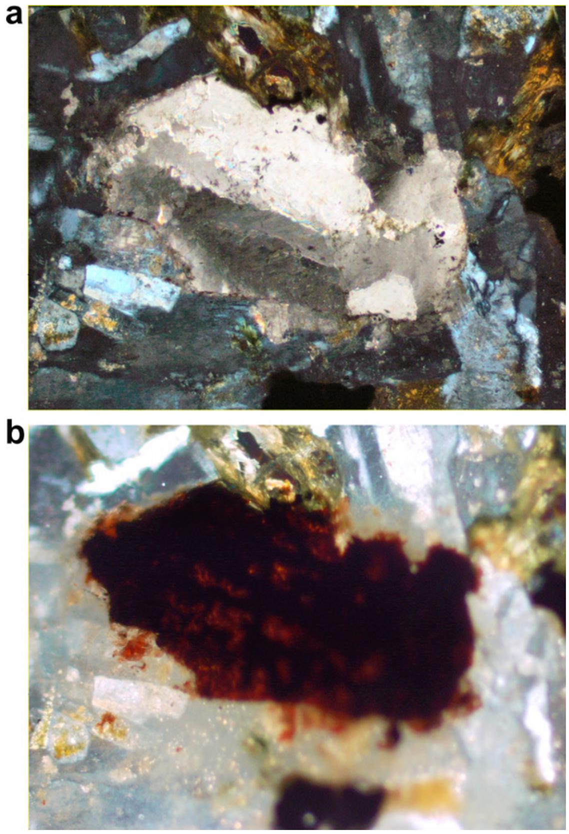


Fig. 4. (a) Siderite in thin section showing minor alteration, before immersion in alkaline solution, WOF = 0.9 mm, XPL. (b) Siderite in thin section showing high degree of alteration after 90 days immersion in alkaline solution, WOF = 0.9 mm, XPL.

### 3.2. Outdoor exposure

After three years of outdoor exposure, there was no visible changes in the surfaces of concrete and mortar slabs prepared with coarse aggregates from Mt Gibralter, as shown in Fig. 5a and b.

### 3.3. Details of concrete in the existing structures

Four concrete structures in the Bowral/Mittagong district were inspected. The aggregates used were petrographically confirmed to be local siderite-bearing microsyenite or trachyte aggregates. The details of the concrete structures are given below.

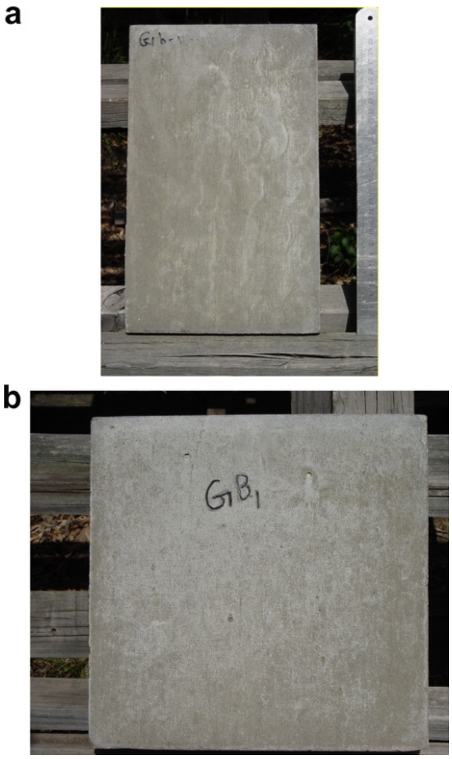


Fig. 5. (a) Surface of a mortar slab after three years exposure. (b) Surface of a concrete slab after three years exposure.

Fig. 6. General view of the Bowral water tank with efflorescence from a joint.

#### 3.3.1. Bowral water tank

This tank was built in an exposed area possibly in the early 1900s, and appears to have been built in a series of horizontal rings using lift formwork. At the time of inspection, there were typical efflorescence patches appearing at numerous horizontal joints, as shown in Fig. 6. The exposed concrete appeared well compacted and the tank was functioning well without any damp patches. There were large patches of orange staining, of unknown origin, mostly running down from the construction joints. It was quite clear that they did not originate from within the concrete. Overall the staining was no more than that expected on similar structures elsewhere.

There was some chipping-off around the edge of the base of the tank that had exposed the aggregate, as shown in Fig. 7. Visual observation of this fracture surface suggested that it had been built using aggregates from the disused quarry at Mt Gibraltar, located adjacent to the concrete tank. A subsequent examination of the sample confirmed that it was petrographically similar to the microsyenite rocks at Mt Gibraltar.

Fig. 7. Exposed aggregate at base of water tank.

Fig. 8. Bowral Austral office building with external walkway (slab).

### 3.3.2. Bowral Austral office building

An office building (ca 1930), believed to be built with concrete made with Mt Gibraltar aggregate was also examined. Aggregate particles collected showed similar features to rock sampled from Mt Gibraltar. As seen in Fig. 8, the top part of the walkway slab and its edge on the side of the building are well exposed to the weather. As shown in Fig. 9, no staining was observed.

### 3.3.3. Mittagong bypass pavement (road shoulder)

The shoulder and the CRCP were constructed in the early 1990s (Fig. 10). The road shoulder is cast from concrete with a coarse siderite-bearing trachytic aggregate sourced from the nearby Nattai River Cut 5. At the time of inspection, the concrete of the road shoulder showed no visible cracks or staining (Fig. 11).

### 3.3.4. Demolished bridge on Mittagong Bypass

A bridge on a nearby section of the CRCP was demolished due to excessive movement of the foundation. This bridge was built at the same time as the CRCP, i.e. in the early 1990s. The concrete pieces showed no staining on the finished surface. Petrographic examination of the concrete revealed that the coarse aggregate in this concrete was composed of a fine-grained "trachyte" containing secondary mineral siderite in similar proportions and texture to that of the rock sample from the Nattai River Cut 5.

Fig. 9. Close-up of the office building slab near door.

Fig. 10. Road shoulder of a section of Mittagong Bypass (built in the early 1990s).

Fig. 11. Road shoulder built with Nattai River Cut 5 aggregate, free of cracks and staining.

At the time of inspection, none of the four structures exhibited any rust staining due to the presence of the secondary mineral siderite. For the three intact structures, no obvious deterioration due to excessive deformation was observed.

### *3.4. Petrographic studies of concrete samples*

In addition to the visual examinations of the structures, detailed petrographic studies of an old (about 80 years old) concrete curb sampled from the Mt Gibraltar quarry were also carried out. Prepared polished thin sections were examined under the petrographic microscope in both polarised (XPL) and unpolarised light (UPL). The aggregate in the concrete was identified as an alkali feldspar microsyenite with interstitial pyroxene (aegirine–augite), siderite and plagioclase feldspar, identical to the rock sampled from the disused Mt Gibraltar quarry. The petrographic study also indicated that the oxidation of the siderite was varied, but most crystals showed a high degree of peripheral (Fig. 12) and internal (Fig. 13) alteration to iron oxides/hydroxides.

A similar petrographic study was also carried out on concrete sampled from the demolished highway bridge near the Nattai River. The aggregate was sourced from the Nattai River Cut 5 and was a fine-grained trachyte containing the secondary mineral siderite. Petrographic studies revealed that although finer-grained with a dominant volcanic (lath-like) texture, it was mineralogically similar to rock at Mt Gibraltar. It also indicated that the general oxidation state of the siderite in the concrete was much less pronounced than found in the old concrete curb sample from Mt Gibraltar, probably due to its younger age (9 years).

Figs. 12 and 13 are images from the petrographic study of the aggregate in concrete (or siderite in a high pH concrete environment), and they clearly show evidence of the oxidation of siderite. The performance of aggregate in a concrete environment or the oxidation of siderite in a concrete environment is critical for the performance of concrete; however it is important to study the performance of siderite in atmosphere, as that governs the performance in concrete.

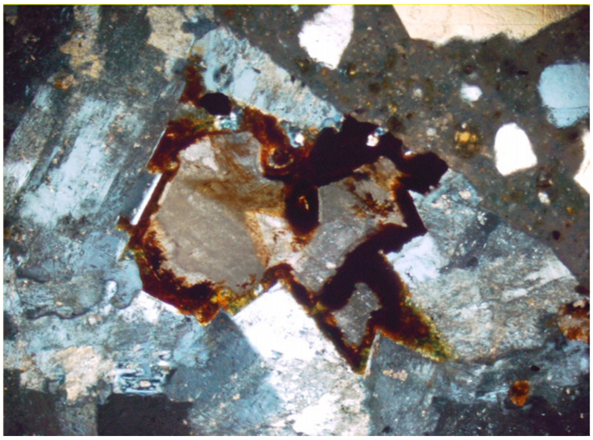


Fig. 12. Peripheral oxidation of siderite on outer surface of aggregate, WOF = 1.75 mm, XPL.

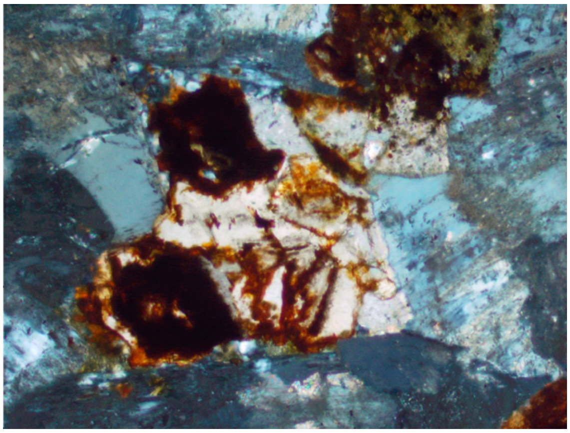


Fig. 13. Internal oxidation of siderite in middle of aggregate, WOF = 0.9 mm, XPL.

### *3.5. Influence of basicity and oxidation potential*

Theoretical studies were carried out to establish the stability of siderite in the atmosphere and also in the concrete environment. The potential to oxidation of siderite depends on the basicity (pH), oxidation potential (Eh), and total dissolved carbon, iron and sulphur in the pore water of the concrete. Thus, the influence of carbon dioxide on the oxidation of siderite was established.

Under atmospheric conditions where the partial pressure of $CO_2$ is 0.0003 atm, siderite has a very small stability field (pH from 5 to 7, Eh from –0.25 to –0.1) (Fig. 14a), and thus will be oxidized to hematite ($Fe_2O_3$), goethite ($FeO(OH)$) or $Fe(OH)_3$, depending on the amount of water in the system and following equations give the chemical reactions. The thermodynamic data used for the calculation of the Eh–pH diagrams (Fig. 14) and the equilibrium constants for the following reactions are from Lawrence Livermore National Laboratory thermodynamic database [5]

$$4FeCO_3 + O_2(g) = 2Fe_2O_3 + 4CO_2(g), \quad (\log K = 61.3) \tag{1}$$

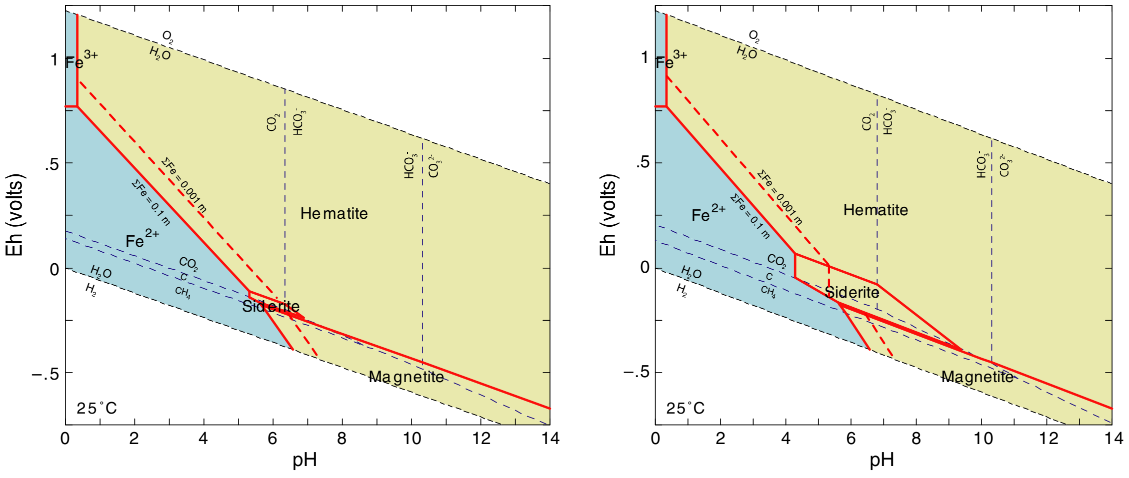
$$FeCO_3 + 2H_2O + O_2(g) = 4FeO(OH) + 4CO_2(g), \quad (\log K = 59.4) \tag{2}$$

$$4FeCO_3 + O_2(g) + 6H_2O = 4Fe(OH)_3 + 4CO_2(g), \quad (\log K = 38.9) \tag{3}$$

Both $FeO(OH)$ and $Fe(OH)_3$ are metastable phases. The stable oxidation resultant phase is hematite, as the following reactions indicate:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O, \quad (\log K = 11.2) \tag{4}$$

$$FeO(OH) = Fe_2O_3 + H_2O, \quad (\log K = 0.96) \tag{5}$$



**(a) Atmospheric conditions ($\log f_{CO_2} = 10^{-3.5}$ atm).**

**(b) In the presence of carbon dioxide ($\Sigma C = 0.1$ molar).**

Fig. 14. Eh–pH diagram of Fe–$CO_2$–$H_2O$ system at 25 °C. The thick solid lines show the boundary between Fe minerals and aqueous species at $\Sigma Fe = 0.1$ m, and the thick dashed lines show the boundary between $Fe^{2+}$ and minerals at $\Sigma Fe = 0.001$ m. The fine dashed lines define the boundaries between carbon species and the stability field of water.

If the pore water in the concrete contains a considerable amount of carbon (as $HCO_3^-$ when pH 7–10), reactions (1)–(3) will favor the left-hand sides, and therefore enhance the stability of siderite. For example, the stability field of siderite in equilibrium with 0.1 m total dissolved carbon is in the range of pH from 4.5 to 9.5 and Eh from –0.4 to 0.1 (Fig. 14b) – much larger than in Fig. 14a.

Thus, it can be seen that in the presence of $CO_2$ there is a tendency for siderite to convert to metastable iron oxides/hydroxides under the Eh–pH conditions of a typical concrete environment, where pH is approximately 10–14. However, it should be noted that these theoretical calculations do not give any information about the kinetics of the reaction nor the rate of oxidation of the siderite; clues to the rate of reaction can be inferred from the field or from accelerated weathering studies. The study also established that the stability of siderite will not change in the presence of 3% NaCl solutions.

## 4. Discussion

The visual examinations of Mt Gibraltar rock slices and the petrographic studies of polished thin sections, after accelerated exposures, confirmed that the siderite secondary mineral was susceptible to alteration through oxidation processes to iron oxides/hydroxides. The rate and extent of such alteration was quite variable, even within the same specimen. It was generally found that the oxidation rate of the siderite was slow in cyclic wetting and drying in both the water and saltwater baths at 38 °C, moderate in the enclosed weatherometer, and rapid in full immersion in alkaline solution. Except for the alkaline immersion, the concrete and mortar slabs showed negligible surface alteration with respect to staining. Although the in situ oxidation of the siderite in the accelerated laboratory experiments was quite noticeable, in the form of pinhole-sized rust spots on the surface of the polished rock slices, the mobility of the iron and subsequent deposition (external staining) on rock and concrete surfaces was negligible. The various exposures were sufficiently severe to cause other surface deteriorations beyond what is commonly experienced in the field, even for the control concrete. The absence of rust staining was considered indicative of the likely long-term performance. In addition, the concrete and mortar slabs also showed no staining after three years of outdoor exposure in Sydney. The accelerated results were fully supported by the theoretical study of the stability of siderite at various oxidation potentials and pH conditions, including the pH range expected in concrete.

Field inspections of four concrete structures with a range of service lives from 9 to 80 years in the Bowral and Mittagong regions revealed no staining or any signs of structural inadequacy. Petrographic examination of concrete samples from the demolished bridge at Mittagong Bypass and a concrete curb from the disused quarry at Mt Gibraltar confirmed the sources of rock used as coarse aggregate in the four structures. They also revealed that although the siderite minerals showed some degree of in situ oxidation to iron oxides/hydroxides, especially towards the periphery of the aggregate, there was no associated staining on the exposed surfaces of the concrete, nor any concentration of iron on the aggregate-paste boundaries.

The findings from the accelerated tests were in full agreement with the field studies where no staining were observed.

## 5. Conclusion

The findings clearly demonstrate that the siderite secondary mineral in the microsyenites and trachytes from the Bowral/Mittagong district are susceptible to alteration through oxidation processes to iron oxides/hydroxides. However, there is no evidence that it causes any adverse staining when used as an aggregate in concrete. Also, it has been demonstrated that the accelerated weathering techniques developed for this study can be used in future assessments of quarried rock during the various phases of any investigation.

## Acknowledgments

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