oxidation | Roofing Slate

roofingslate.wordpress.com/tag/oxidation

Quality factors in slates – Part I

Traditionally, the slate market has offered a wide variety of **different qualities** of slate. Each manufacturer has their own commercial references depending on the characteristics of its outcrops, so the market is full of specific commercial references, generating to a general confusion. The first class slate from a company may be very different from the first class of other company. In general, the quality criteria are similar for the entire sector (no alterable minerals, adequate thickness, uniform exfoliation, etc.), although it is the final use of the slate tiles which really define the specific requirements. For example, slate tiles used in **Pyrenees**, where the roof has to support the weight of the snow many days per year, have high thickness (8-12 mm), regardless of the presence of weatherable minerals. On the other hand, slate tiles used in **Brittany**, France, must be much more thinner (3-7 mm), without weathering minerals and smooth, uniform appearance. Broadly speaking, the different commercial varieties can be grouped into first, second and third quality, although there are plenty of references intermediate (*rustic, first/second/third special quality, first/second economic, second selection, historical monuments selection*, etc…).

The factors that determine the quality of a slate tile can be divided into three groups: **petrological**, **tectonic** and **productive**.

Petrological factors

These factors are referred to the mineral components of the slate and the spatial relationships among them.

Mineralogical composition

Slate is composed mainly of **quartz**, **chlorites** and **mica**, together with some other minerals present in variable amounts, like feldspars, chloritoid, tourmaline, carbonates, iron sulphides, etc. However, specific mineralogy depends on the petrological variety of the roofing slate (slate s.s., shale, schist, etc).

For slate s.s., the most typical variety of roofing slate, the average mineral proportions determined by different authors can be found at Table 1. Generally speaking, a **good slate** should have between 10 and 50 % quartz, 15 – 60 % chlorite and 20 – 70 % mica. Minor minerals like tourmaline, zircon, rutile, leucoxene and chloritoid are not important. Only

Autor	Q	Chl	Ms	Cld	Op	Cto	Fto	Otras
(Lombardero y Quereda, 1992)	22-25	15-27	40-55					< 5
(Rodríguez-Sastre y Calleja, 2004)	35	15	40		7		2	< 1
(Lombardero et al., 2002)	22-25	15-20	40-60	0-10		0-10		Ab, Rt, Tur
(García-Guinea et al., 1997)	22-25	15-20	40-60	0-10				
(Ward y Gómez-Fernandez, 2003)	17-43	12-34	29-56				1-24	Pg, Anl
(Fraser-Española, 1975)	31-45	6-18	38-42		3-6			Rt
(Cárdenes et al., 2008a)	7-27	18-43	31-51	0-17			4-11	

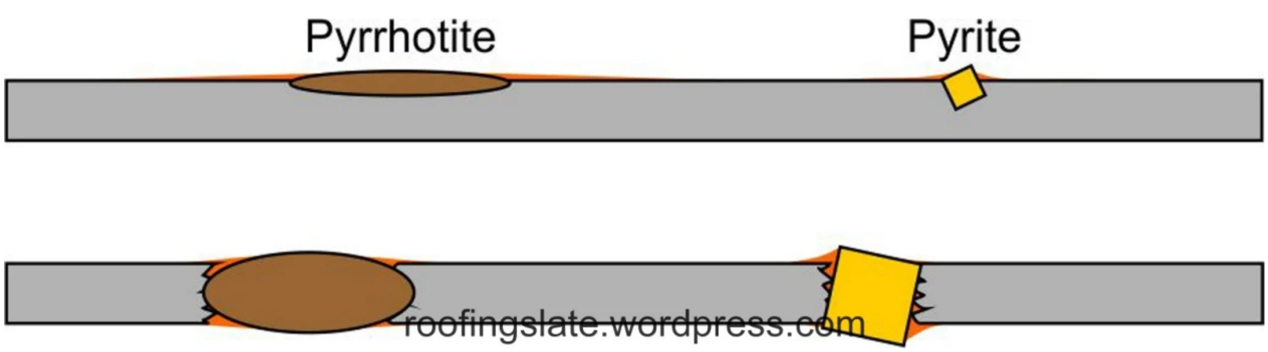
carbonates and iron sulphides could affect the quality of the slate. Graphite fragments may also have some effect on slate quality by favoring oxidation processes, but only if there are iron sulphides in the slate. Further explanation on weathering of these two minerals can be found at their correspondent posts (oxidation and gypsification). Also, further explanation on slate mineralogy can also be found here.

Other petrological factors related with roofing slates quality are grain size, textural homogeneity and presence of sedimentation beds. These factors will be explained in following posts.

Pathologies – part III

Acting against oxidation

Above all, it must be remembered that oxidation is a purely aesthetic defect, which does not involve the loss of the roof **waterproofing**. Only in exceptional cases, where the size of the iron sulphide is greater than the plate thickness, the oxidation can break it.



Up: Lateral view of a slate tile, in which the thickness of the iron sulphides is lower than the thickness of the tile itself
Down: The thickness of the iron sulphides is now higher that the thickness of the tile, breaking it when the oxidation develops

It is also necessary to know the **susceptibility** of the slate to oxidation. An experienced technician will have no problem recognizing the existence, abundance and types of iron sulphides present, so it is possible to estimate the **oxidizability** of a slate variety quite rightly. Also, **preoxidation** treatments with $\mathbf{H_2O_2}$ can be very illustrative, although the attack conditions must be carefully checked for no erroneous results.

In recent years there have been proposed two types of oxidation treatments, **application of chemical products** and **passivation** of the iron sulphides. The application of chemicals products is done in huge treatment stations located in the same slate producing factory.

These products have several disadvantages to be considered, during the application stage and with the effective protection they can give to the slate. Still, there are already slate producing companies applying this type of products, albeit in a restricted way.

The other type of treatment involves **selectively attacking** the iron sulphides, weathering first their surface and then coating them with an inert mineral crust that protects against the environmental conditions. This method is effective in theory, and it has not been developed for practical use yet, so its real effectiveness can´t be known.

Experimental roof with tiles of slate treated with different products and treatments

As a general recommendation, against oxidation on the roof, we should act calmly, first weighing the extent and type of damage, and then considering the possibility of changing the affected tiles. Each case is different, and not always the oxidized tiles are negative. In **restoration** of historic monuments it is common to search for oxidized tiles to replace the originals. Also in **modern buildings**, rusted slate offers new attractive textures and colors.

Further reading:

Passivation techniques to prevent corrosion of iron sulphides in roofing slates

Oxidación de sulfuros en pizarra ornamental: tratamientos protectores con siloxanos

Protocolo de valoración de la efectividad de productos protectores de pizarra para cubiertas

Sealant composition for roofing slate

Pathologies – part II

Oxidation

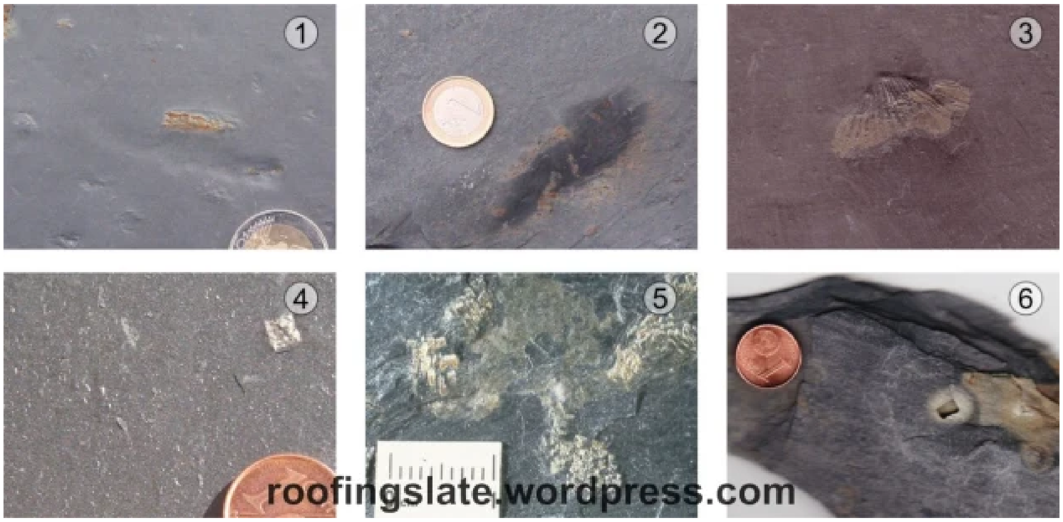
Iron oxidation consists of the change of Fe^{2+} to Fe^{3+}, by the gain of an electron. In roofing slates, most important iron minerals are **iron sulphides**, being the most abundant **pyrite** (FeS_2), which is oxidized in the presence of oxygen according to the reaction:

$$FeS_2 + O_2 \rightarrow Fe^{2+} + 2SO^{2-}{}_4 + H^+$$

The oxidation of these iron sulfides is favored by **acid urban environments** and **coastal areas**, where sea salts favor oxidation reactions.

However, not all the iron sulfides oxidize in the same way. There are several types of iron sulfides, such as **pyrite**, **pyrrhotite**, marcasite, arsenopyrite, etc, being the two firsts the most abundant by far. Each iron sulphide has a different structure. Thus, the oxidation susceptibility depends on the strength of this mineral structure. For example, **pyrrhotite** has a poorly ordered **hexagonal** structure, being more vulnerable to oxidation than the **pyrite cubic** structure. In real world, most oxidations developed in roofing slates are due to pyrrhotite, so it is very important to distinguish between these two minerals, since the oxidability of the slate depends on it.

Finally, the occurrence of **organic matter** in the slate favors the oxidation, due to the increase of acidity during its decomposition.



1 – Pyrrhotite, brown color, with not recognized shape. 2 – Pyrrhotite partially oxidized together with an inclusion of organic matter. 3 – Pyrrhotited fossil of a bivalve. 4 – Cubic pyrite crystal. 5 – Cubic pyrite crystals forming aggregates called framboids. 6 – Footprint of a disappeared cubic crystal of pyrite oxidized.

Further reading: Determination of iron sulphides in roofing slates from the north west of Spain

Pathologies – part I

Pathologies in roofing slates

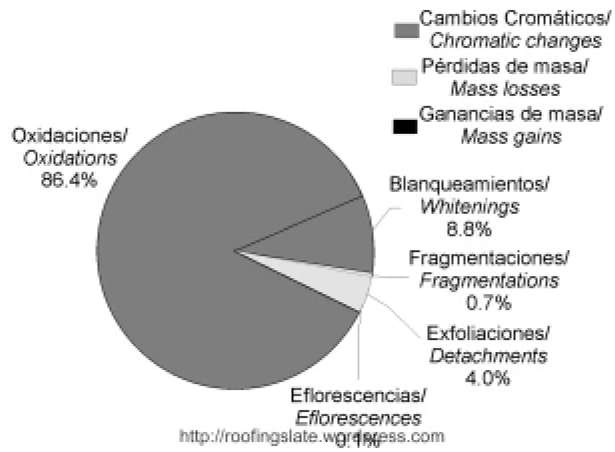
The pathologies formed in slate roofs are mainly due to the presence of potentially unstable minerals (**iron sulfides, carbonates and organic matter**). These minerals may become altered by the effect of environmental agents, once the slate roof is finished. The pathologies are mainly associated with **oxidation** and **gypsification** processes of the cited mineral phases.

The **oxidation** is generated when the iron sulfides which may contain the slate became weathered, forming **iron oxides**. This forms reddish rust marks on the surface of slate tiles. This is mainly an aesthetic defect, as only rarely slate tiles disintegrate due to oxidation. However, it is the main fact in volume of complaints from slate customers (Figure 01). The presence of tiny fragments of **organic matter** may favor the oxidation processes.

The **gypsification** occurs when the carbonates react with the environmental SO_2, forming **gypsum**. In this case, gypsum has larger size than carbonates, so a swelling may occur within the slate tile, causing it to disintegrate. Despite this, the incidence that this pathology in the customer complaints is significantly lower than oxidation, maybe since it is not as striking (Figure 01).

There are also other characteristic pathologies and minor defects but also must be taken into account.

Following the criteria dictated by **ICOMOS**, defects and pathologies found in roofing slates can be classified into 3 groups (Table 01).



Customers complaints by volume of monetary costs

	Agent	Mechanism	Pathology
Mass losses	Acid environmental conditions	Mechanical (gelifraction) or chemical disaggregation (new mineral phases), temperature changes, joints breaks	-Detachments -Fragmentations
Mass gains	Atmospheric contamination, biological agents	Formation of new mineral phases, growth of lichens or mosses	-Efflorescences -Biological colonization
Chromatic changes	Acid or salt environment, roof elements	Oxidation of iron sulfides, gypsification, alteration of roof elements	-Oxidation -Whitening

Most common pathologies in roofing slates