



Use of sulfidic tailing residue for underground cementitious concrete



ESR13 Natália Pires Martins
Main Supervisor: Dr. Guillaume Habert
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#1 Objectives, milestones, deliverables

Objectives

The objective is to develop a cementitious material based on sulfidic tailings

- Development of calcium sulphoferrite cement
- Early stage deflocculation with mineral admixtures
- Rheology control

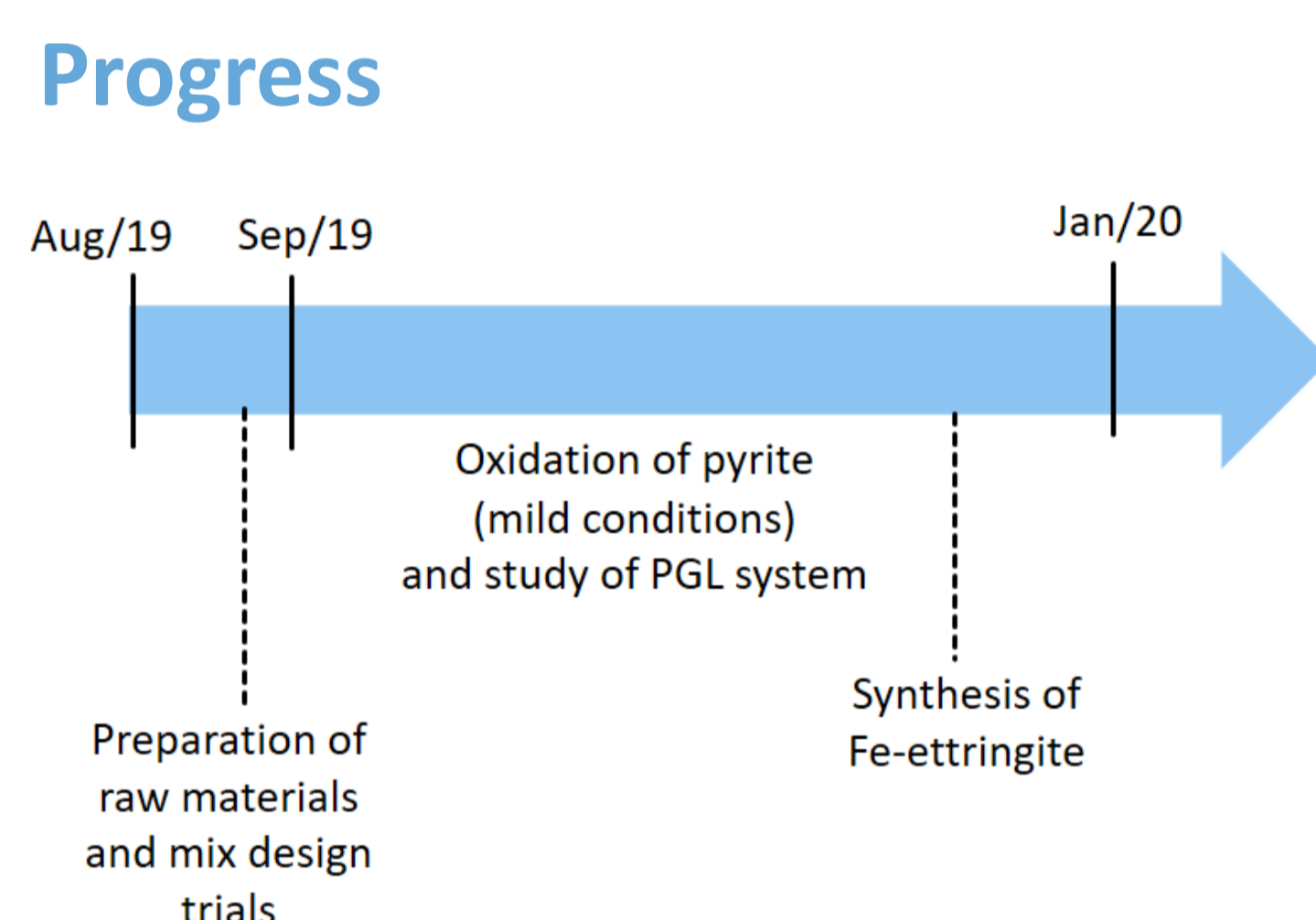
Milestones

- deflocculation of tailing with mineral admixture and sulphide oxidation to produce calciumsulphoferrite cement (M24);
- combination of both reactions and rheology control of flowable tailing concrete with medium mechanical properties (compressive strength 5 MPa and reduced shrinkage 0.001) (m3.3) (M40).

Deliverables

- 02 peer-reviewed papers
- Confidential report summarizing all results

Figure 1. Main activities developed over the past six months, within Task 2: development of binder based on the oxidation of sulphide minerals.



#2 Research

Methodology

1. The starting point for the mix ratios was driven by thermodynamic calculations performed in the software GEMS [1]. The default database of GEMS and CEMDATA18 [2] were used. To simulate the extent of oxidation of pyrite, O₂ was added to the system in steps.

2. Sample SUL_GM_08 was dry-milled in agate mortar grinder (d₅₀<1μm) and put under mild oxidizing conditions before being mixed with lime, gypsum and water and aged for 14 days. Oxidation of pyrite and mineralogy of the PGL mix were followed by powder diffraction using a Bragg-Brentano X-ray diffractometer (D8 Advance, Bruker AXS, Germany) with CoKα radiation (λ = 1,79026 Å). Qualitative phase analysis was carried out on the software DIFFRAC.EVA (Bruker AXS) and PDF-2 database. Semi-quantitative analysis performed on Profex [3]).

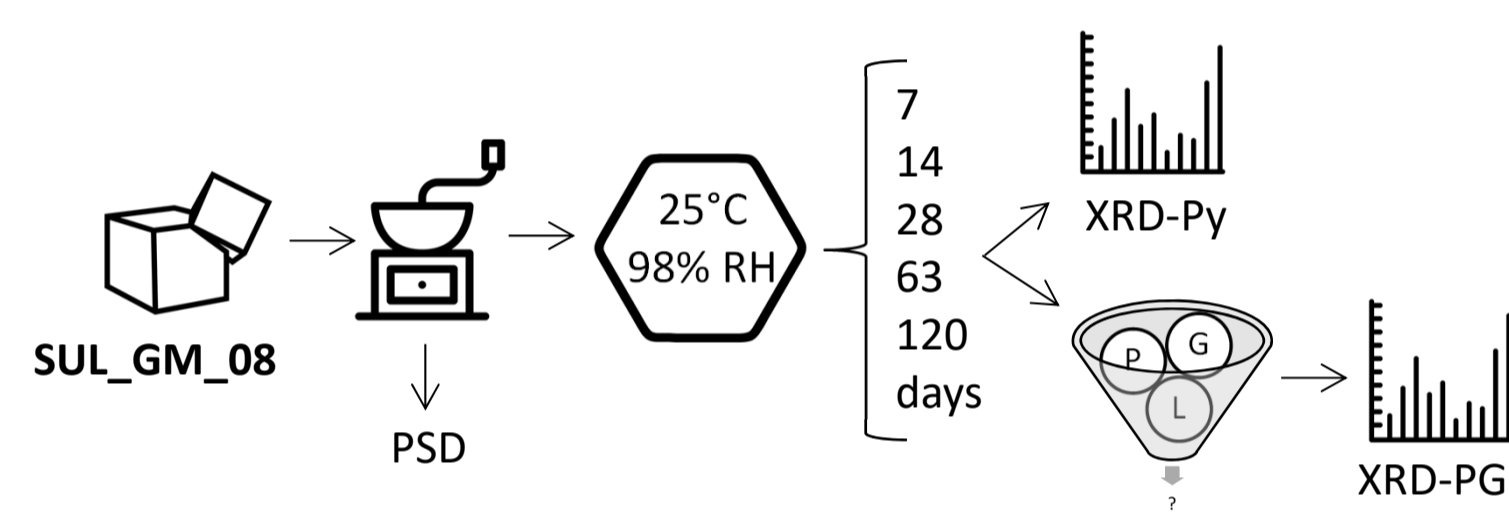


Figure 2. Scheme of methodology used to study a system composed of P (oxidizing FeS₂), G (CaSO₄·0.5H₂O) and L (Ca(OH)₂).

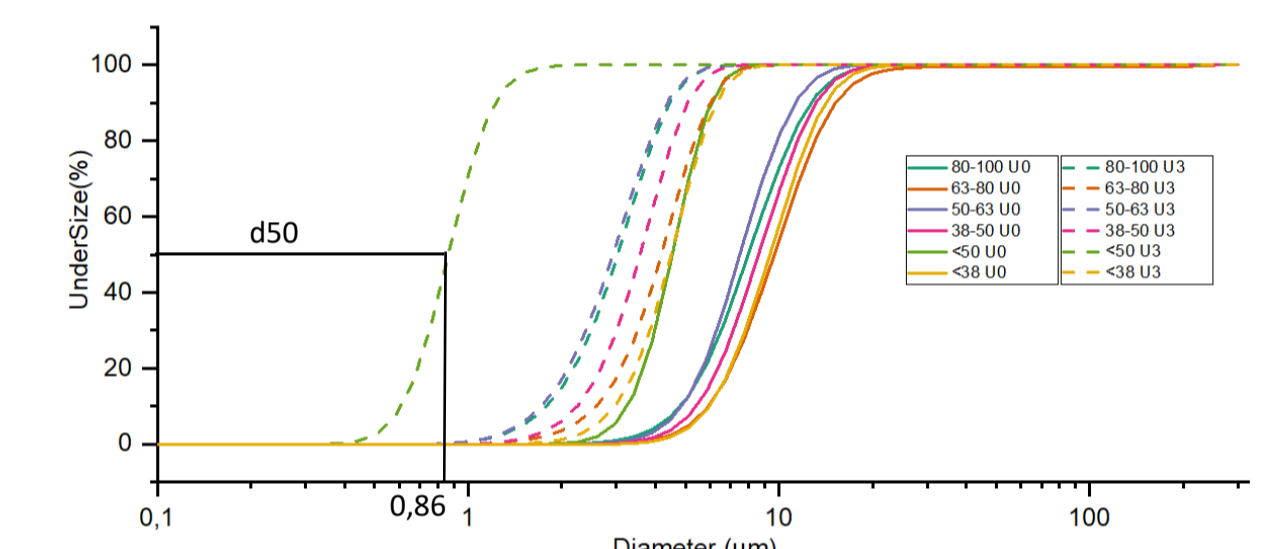


Figure 3. Particle size distributions obtained by laser diffraction on samples.

3. Fe-ettringite was synthesized using the method described by [4]. Solids were vacuum filtered and kept in a dessicator at low vacuum until constant mass was reached, when they were gently ground in agate mortar and underwent powder XRD using the previously described settings.

#3 Conclusions

Even ground to an extremely fine powder (d₅₀<1μm), pyrite has not oxidized after 120 days of exposure to humid air at room temperature.

Pure Fe-ettringite has been successfully synthesized from CaO and Fe₂(SO₄)₃·5H₂O. However, its formation on the PGL mix was not observed, nor the formation of other iron-containing phases detectable by XRD.

#4 Upcoming steps

- Follow pyrite oxidation at longer exposure times under mild conditions.
- Employ accelerated oxidising conditions.
- Utilize oxidation products on the mixtures to overcome delay in oxidation.
- Secondment at VITO (March-June/2020): hydration studies on mixtures of cement (CSA, CA, PC) and pyrite oxidation products.

References

- D.A. Kulik, GEMS-PSI 2.3, PSI Villigen, Switzerland, 20098 available at <http://www.ies.web.psi.ch/Software/GEMS-PSI/index.html>.
- B. Lothenbach, D.A. Kulik, T. Matschei, M. Balonis, L. Baquerizo, B. Dilnesa, G.D. Miron, R.J. Myers, Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials, Cem. Concr. Res. 115 (2019) 472–506. doi:10.1016/j.cemconres.2018.04.018.
- Doebelin, N. and R. Kleeberg, Profex: a graphical user interface for the Rietveld refinement program BGMN. Journal of Applied Crystallography, 2015. 48(5). <https://doi.org/10.1107/S1600576715014685>
- R.L. Norman, S.E. Dann, S.C. Hogg, C.A. Kirk, Synthesis and structural characterisation of new ettringite and thaumasite type phases: Ca₆(Ga(OH)₆-12H₂O)₂(SO₄)₃·2H₂O and Ca₆[M(OH)₆-12H₂O]₂(SO₄)₂(CO₃)₂, M = Mn, Sn, Solid State Sci. 25 (2013) 110–117. doi:10.1016/j.solidstatesciences.2013.08.006.

Results

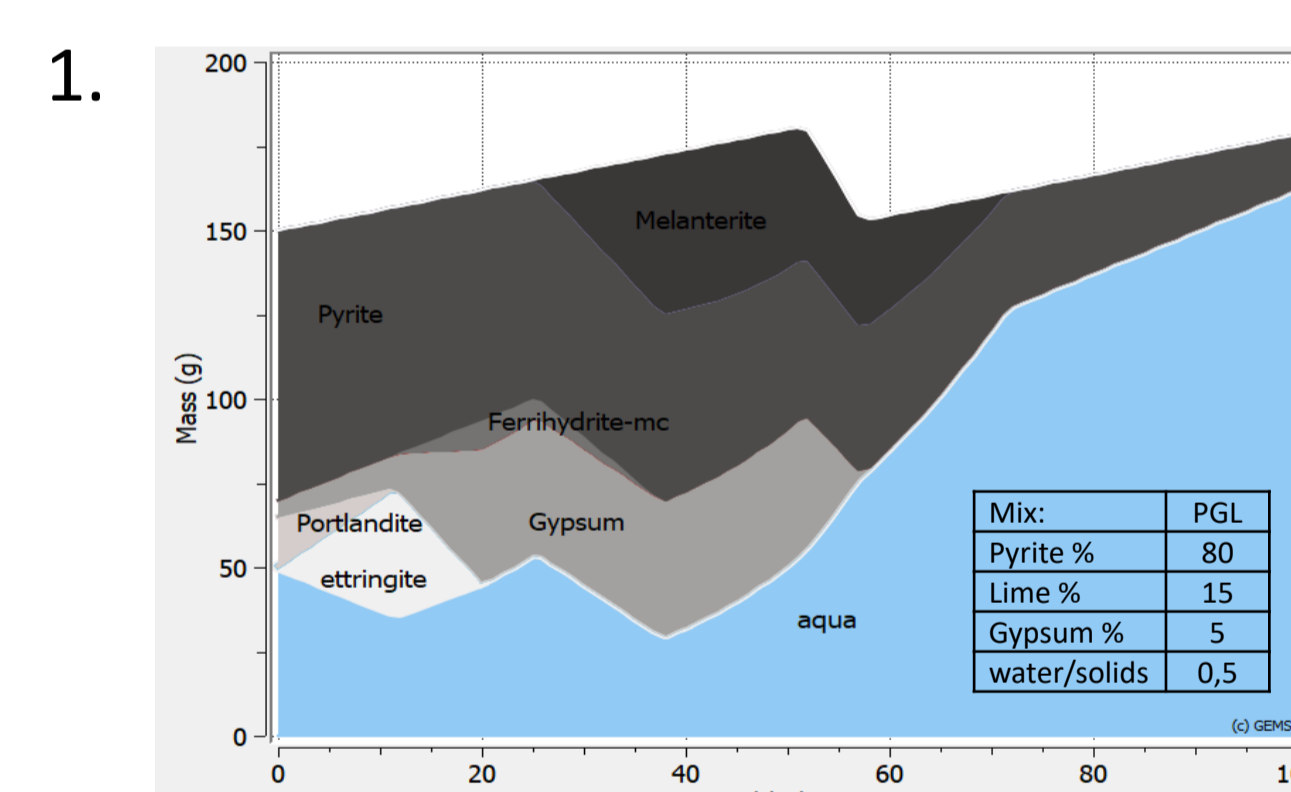


Figure 4. Phases formed in the system composed of P (oxidizing FeS₂), G (CaSO₄·0.5H₂O) and L (Ca(OH)₂) at different extents of oxidation of pyrite. The iron analogue of ettringite should form at an optimum extent of oxidation. Formation of the thermodynamically stable iron oxides was prevented in the model.

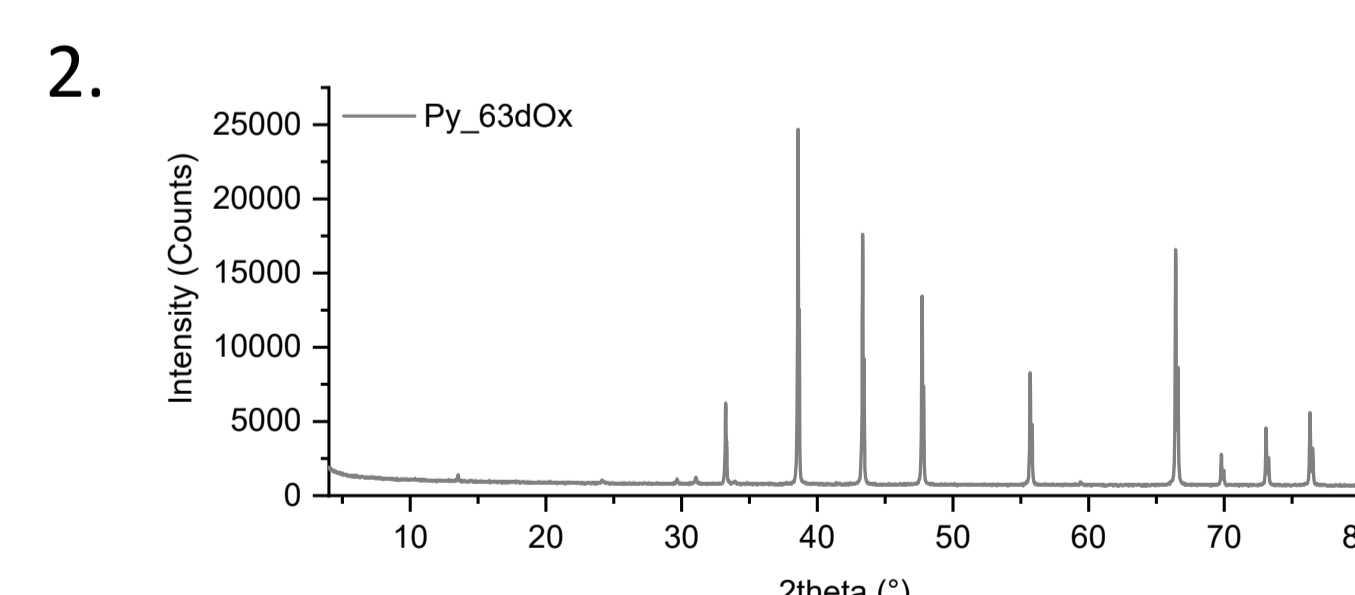


Figure 5. Powder diffraction pattern of pyrite sample kept in the chamber for 63 days (Py_63dOx).

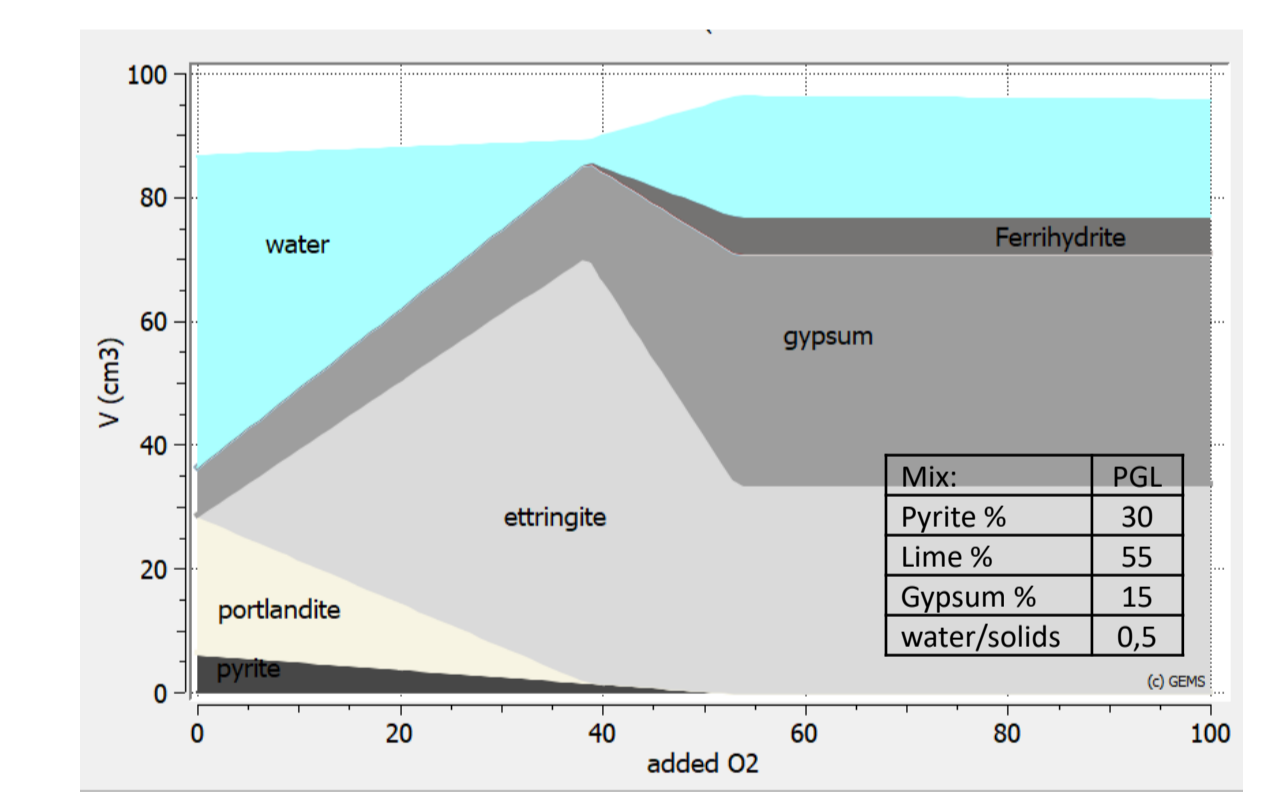


Figure 6. Powder diffraction pattern of PGL produced from Py_63dOx.

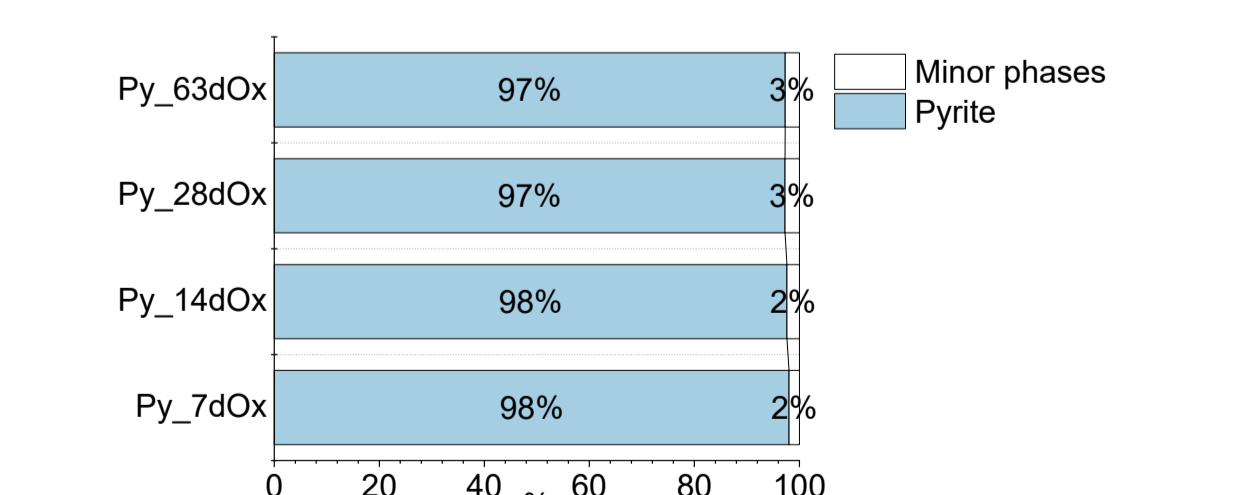


Figure 7. Results of semi-quantitative analysis [4] performed on XRD patterns of pyrite samples kept in the climate room for 7, 14, 28 and 63 days.

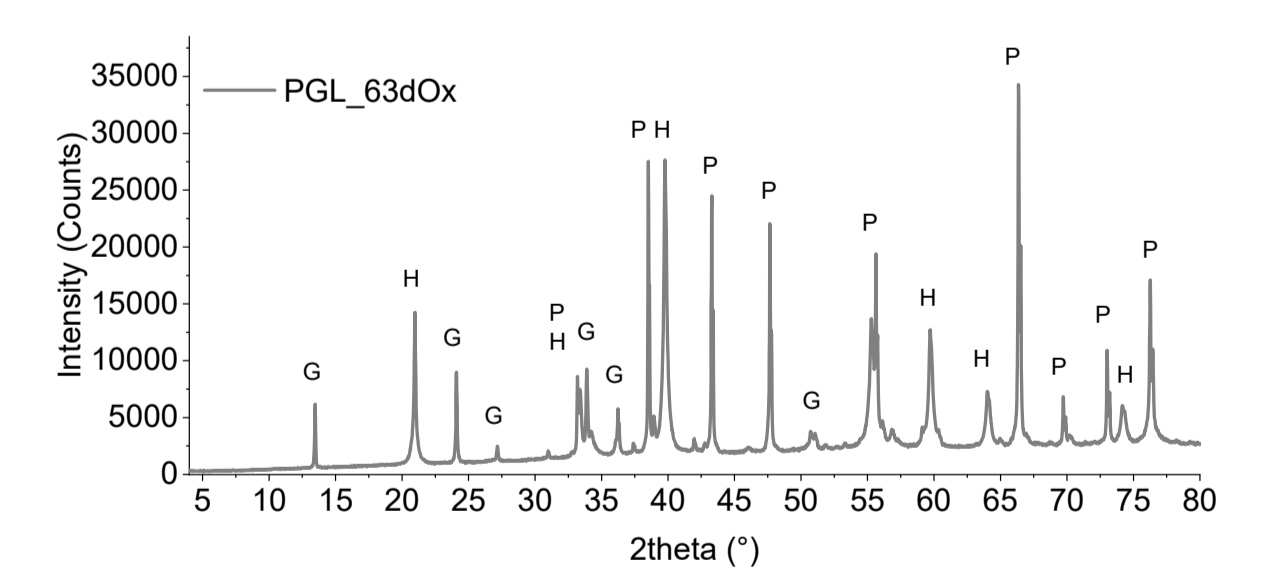


Figure 8. Results of semi-quantitative analysis [4] performed on XRD patterns of PGL produced from samples of pyrite kept in the climate room for 7, 14, 28 and 63 days.

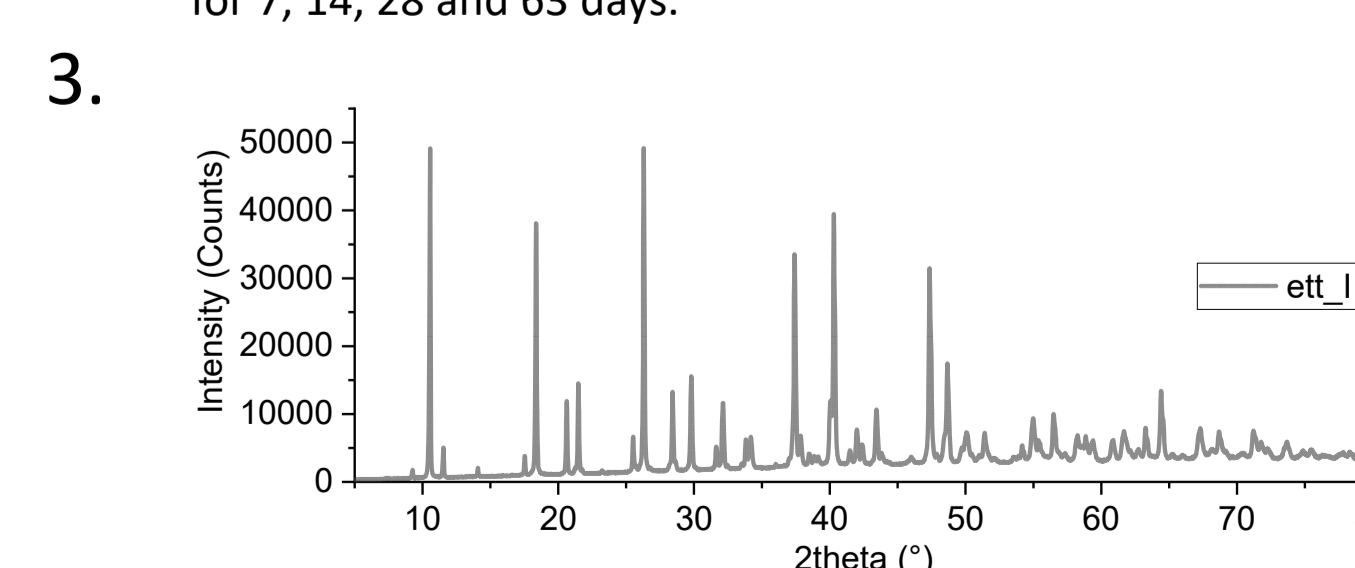


Figure 9. Powder diffraction pattern of solids formed. All peak positions match the reflections of Fe-ettringite structure ICSD 251757 (phase pure, according to semi-quantitative).

