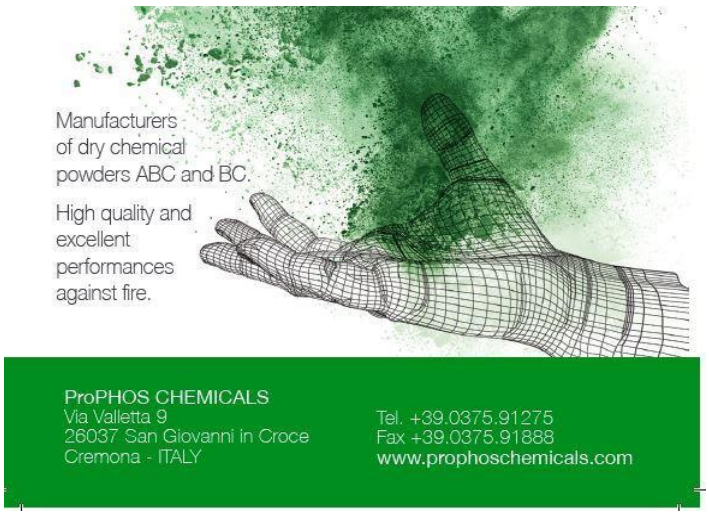

PHOSave

Deliverable D3.2

Sample of at least 100 g of magnetic materials obtained from functionalized NPs

Partner responsible:

Part no.	Participant organisation name	Short name	Country	Nature
1	ProPHOS Chemicals S.r.l	**ProPHOS**	Italy	**SME**

Table of Contents

REPORT OF THE ACTIVITY CONDUCTED BY POLITECNICO DI MILANO

SYNTHESIS AND SCALE-UP OF FUNCTIONALIZED MAGNETIC MICROAGGREGATES

The magnetic microaggregates that were used to treat Exhausted Extinguishing Powder (EEP) have been synthesized following the co-precipitation method starting from Fe^{2+} and Fe^{3+} salts at atmospheric pressures and temperatures between 50 and 80 °C. The subsequent functionalization of the obtained magnetic particles can be performed in mild conditions and allows the addition of a proper coating that makes them amphiphilic. This means that the magnetic NPs are completely dispersible in water, but also exhibit the desired affinity with the silicon oil that must be removed from the extinguishing powders. The synthesis can be either performed on a laboratory scale, but also on a larger scale. In this sense, the synthesis of differently functionalized magnetic NPs is currently being optimized in a 20 l pilot plant at Politecnico di Milano (see Fig. 1).

Figure 1: 20 l capacity pilot plant installed at Politecnico di Milano.

The scale up of the process currently allows the synthesis of the product in amounts larger than 100 g, as shown in Fig. 2.

Figure 2: Typical batch of amphiphilic magnetic particles used.

The obtained product is constituted by an aqueous dispersion of functionalized magnetic particles, with an average size of 10 μm. This assures a high porosity of the particles and consequently an extremely high surface area exposed to the environment. The magnetic particles have been characterized by means of a combination of optic microscopy and dynamic light scattering (hereinafter DLS); the results of the analysis are reported in Fig. 3.

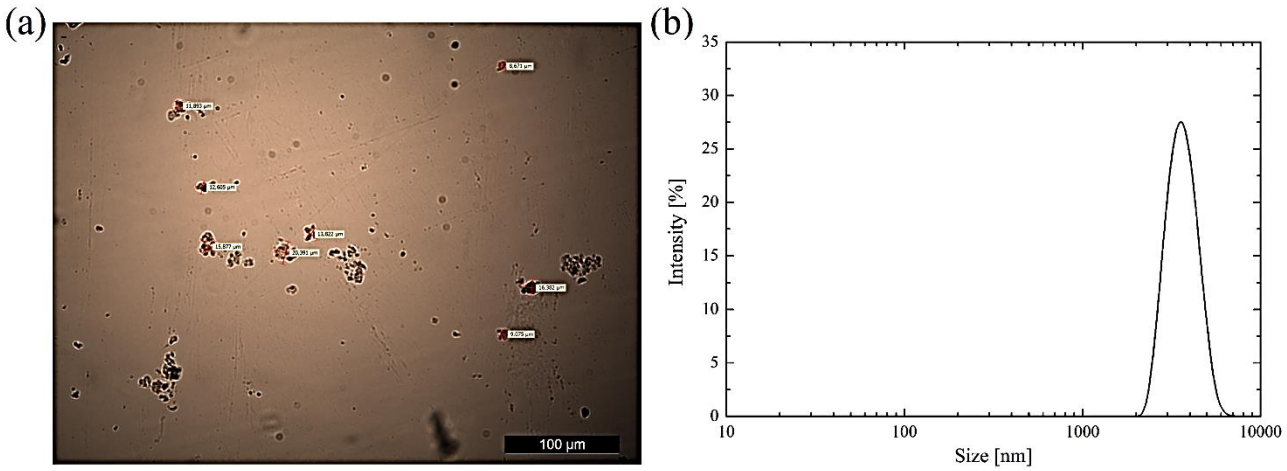

Figure 3: (a) Optic microscope image and (b) particle size distribution obtained via DLS for the produced magnetic particles.

More in detail, Fig. 3a shows the optic microscope image, that allows to evaluate the average size of the synthesized product. Fig. 3b reports the particle size distribution as obtained via DLS. In particular, it is possible to notice that the size distribution is very narrow, thus confirming a good homogeneity of the product.

POWDER TREATMENT PROCESS

The treatment process has been performed at room temperature, in a batch, magnetically stirred reactor. More in detail, 10 g of powder, 30 g of solvent (3:1 w/w with respect to the powder) and 1 g of magnetic particles (1:10 w/w with respect to the powder) have been loaded in the reactor. The solvent was chosen among distilled water and acetone. The system was stirred for 30 min and then the solid content recovered via atmospheric filtration. A schematic representation of the process is depicted in Fig. 4.

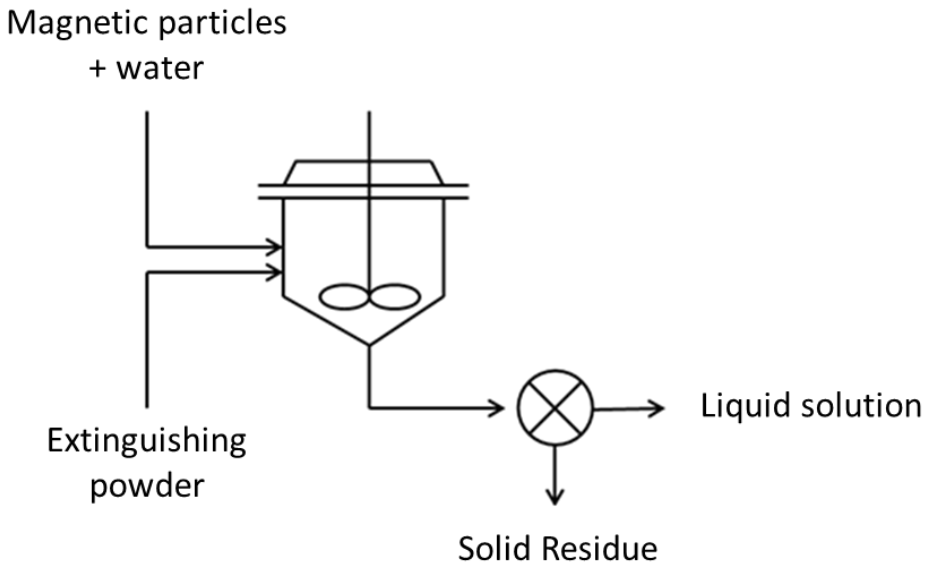

Figure 4. Schematic representation of the process for the powder treatment.

The amount of the recovered powder was evaluated via thermogravimetric analysis (TGA) performed on the filtrate.

TREATMENT WITH WATER AS SOLVENT

Water was used as a solvent both in the form of distilled water and as a solution saturated with MAP, with the idea to avoid the further solubilization of the recovered MAP and to collect it as a solid by means of atmospheric filtration. However, the use of a saturated solution led to a dramatic effect on the magnetic particles, due to the very high ionic strength. Therefore, the use of distilled water as the solvent was investigated.

The material balance between the inlet and the outlet conditions is reported in Table 1.

Table 1: Inlet and outlet weight conditions for the different components in the water-based process.

	INLET [g]	OUTLET [g]
Powder	10.017	7.476
H_2O	30.522	28.104
Magnetic Particles	1.003	
Solid residue (magnetic particles+insoluble components)		3.544
TOT.	41.542	39.124

It is possible to notice that up to 74.6% of the original powder is recovered and completely solubilized in water. 2 g of the solvent are lost during the filtration due to evaporation. The solid residue is attributed to the silica and other insoluble components of the extinguishing powder.

TREATMENT WITH ACETONE AS SOLVENT

Acetone was used as a suitable solvent to grant the dispersion of the magnetic particles, avoiding the solubilization of the powder. The material balance between the inlet and the outlet conditions of the treatment process is reported in Table 2.

Table 2: Inlet and outlet weight conditions for the different components in the acetone-based process.

	INLET [g]	OUTLET [g]
Powder	10.048	7.296
Silicone Oil		0.166
Acetone	30.065	10.904
Magnetic Particles	1.012	
Solid residue (magnetic particles+insoluble components)		3.196
TOT.	41.125	21.562

Here, it is possible to recover a 1.7% (0.166 g) of the original powder dissolved in acetone. This component is the silicone oil layer. A huge amount of acetone is lost during the filtration due to the evaporation, explaining the big difference between the outlet mass compared to the inlet. To evaluate the amount of powder recovered among the residual solid phase, this was re-dispersed in water, to allow its solubilization. After filtration, 72.6% of the original extinguishing powder was recovered in solution.

EXAMPLE OF METAL REMOVAL IN AQUEOUS PHASE

400 mL of contaminated water was treated with an aqueous solution of magnetic particles at 9.5% by weight. Samples were divided into single batches of 50 mL, each with 15 mL aqueous solution of magnetic particles, and stirred for 30 minutes using a vortex. The samples were then placed on a magnet overnight to separate the magnetic particles and obtain purified water. As a verification tool of the effective removal of metals from the water treated, a series of standard tests according to EPA (EPA 6020A 2007) and POM (POM 545 Rev. 1 2013) methods were performed. The results obtained are shown in Table 3.

Table 3: Effectiveness of magnetic particles on metal removal.

METAL	UoM	PRE-treatment	POST- treatment	DLgs 152/06 All. 5 Tab 2	Method
As	µg/l	66,9	2,4	10	EPA
Mn	µg/l	927	22,4	50	EPA
Fe	µg/l	4216	36	200	EPA+POM

CONCLUSIONS

Magnetic microaggregates can be produced starting from iron salts using mild conditions, with a narrow particle distribution. This allows to obtain a product with a very huge active area, but easily recoverable via both the application of a magnetic field or atmospheric filtration. Furthermore, the magnetic particles can be functionalized with proper ligands in order to achieve selectivity towards a particular compound that must be eliminated or recovered. The synthesis process can be easily scaled-up and currently a 20 l pilot plant is being developed by Politecnico di Milano. The properly functionalized magnetic particles have been used in the treatment of the extinguishing powder. Operations were conducted in a batch, magnetically stirred reactor using both water and acetone as the solvent. In both the cases, it was possible to recover about the 75% of the original powder. An example of metal removal in aqueous phase was successfully performed.