

Phosphating of Carbon Steels in Solutions Containing Zinc and Zinc-Manganese Phosphates

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Abstract. The formation of phosphating coatings on carbon steels by novel baths containing zinc and zinc-manganese phosphates has been investigated. By gravimetric, chemical, electrochemical and physical methods are determined the characteristics of preparations (density, pH, conductivity, total and free acidity) and those of the produced coatings (thickness, phase and chemical compositions, structure, protection ability). The concentration range has been varied from 5 to 20% vol., while the temperature effects have been studied in the range from 20 to 80°C. The thicknesses of the coatings and the amount of the substrate dissolved have been determined. It is proved that Mn-phosphate decreases the coating thickness for all working solution concentrations and temperatures, at the same time increases the mass of dissolved metal of the substrate. The results obtained indicate that the coatings developed in zinc and manganese baths contain the following phases: hopeite, phosphophyllite, quasihopeite, strunzite and mixtures of them.

1. Introduction

Phosphating of ferrous and non-ferrous materials is the most widely used surface treatments in practice, due to its easy production, good corrosion resistance, low-cost and excellent adhesion with the next paint or polymer coatings.

The process can be defined as the treatment of a metal surface so as to give a reasonably hard, electrically non-conducting surface coating of insoluble phosphate which is contiguous and highly adherent to the underlying metal and is considerably more absorptive than the metal. The coating is formed as a result of a topochemical reaction, which causes the surface of the base metal to integrate itself as a part of the corrosion resistant film.

The formation of a phosphate coating is a complex process involving consequently dissolution, crystal nucleation and growth with rates and mutual influences affecting the crystallization kinetics as well as the coating structure and properties [1-3].

The most commonly used phosphate coatings are iron phosphate, zinc phosphate and manganese phosphate. In zinc phosphating, the corrosion protection is key, which is increased by the zinc content included. But zinc phosphate is also suitable as a sliding surface. Resilient sliding properties are the main feature of manganese phosphate. The layer reduces friction and is very absorptive for oil, so that it is used for plain bearings and bushings for example. For highly loaded sliding surfaces it is used in preference to the other phosphating methods [4, 5].

The present work reports data on phosphating process of mild steel surfaces with zinc and manganese phosphating solutions (ZnPh and MnPh). The main characteristic such as density, pH, and



conductivity as well as the total and free acidity of the phosphating concentrates were determined. The effects of solution concentration and temperature on the coating thicknesses, phases, structures and elemental compositions were studied. The corrosion resistance and the protective properties of the coatings were determined, too.

2. Experimental

2.1. Materials and methods

2.1.1. Materials and samples. Experimental probes had the form of a square (0.005 m²) and were made of sheet mild steel (0.17% C) 1.0 mm thick. The electrochemical experiments were carried out with plate-shaped specimens prepared in accordance with ISO/FDIS 17475 (ISO 17475:2005) and a fixed working surface area of 1 cm². In addition, samples with a form of a disk (0.001 m²) were used as specimens in case of all physical methods applied in the study.

2.1.2. Solutions. The phosphating solutions are liquid concentrates of zinc and manganese hydrogen orthophosphates and phosphoric acid, containing stabilizing agents and accelerators.

The working media for phosphating were aqueous solutions of the liquid concentrates with concentrations 5.0; 10.0; 15.0 and 20 % vol. The experiments were carried out at temperature 20.0; 40.0; 60.0 and 80°C for 5.0; 10.0; 15.0 and 20 min. The working/model media used for the corrosion experiments is 0.6 M NaCl.

2.1.3. Methods. Gravimetric method. The Gravimetric method was used for studying kinetics of forming and determining conditions of the processes for increasing of the coating's thicknesses depending on the influence of different factors. The method allows determining mass alteration of experimental samples after forming and removing coatings:

$$M = \frac{m_1 - m_2}{S}, \text{ g m}^2$$

where: M , g m² is mass or as accepted to call a thickness of the obtained coating,; m_1 and m_2 are the sample mass after forming and removal of coating, g; S is the sample surface area, m².

Electrochemical methods. Open circuit potential determination. Metals immersed in liquid electrolytes media resulted in establishment of non-equilibrium, i.e. the so-called corrosion potentials. The corrosion potentials are not indicative with respect to the resistance attained but their values and time variations provide enough information about the character of the corrosion process, the behavior of both the metal and metal coating in different media under various conditions.

Potentiodynamic polarization method. The polarization curves recorded potentiostatically or potentiodynamically allow determination of various corrosion characteristics such as corrosion rate, corrosion potential, etc. The experiments were carried out with EG&G Princeton Applied Research, *Potentiostat/Galvanostat, Model 263A*, provided with the specialized software package PowerCORR[®].

Physical methods. Optical microscopy (OM). The microstructure of the coatings were determined by optical microscopy, using a microscope OPTIKA[®] Model: B-500Bi.

Scanning electron microscopy (SEM). The morphology and structure of the coatings were examined by scanning electron microscopy, using a SEM/FIB LYRA I XMU, TESCAN electron microscope, equipped with ultrahigh resolution scanning system secondary electron image (SEI).

Energy dispersive X-ray spectroscopy (EDX). The energy dispersive spectroscopy is a local X-ray spectral analysis which permits qualitative and quantitative determination of surface micro volume contents of the order of several μm³. Apparatus Quantax 200, BRUKER with spectroscopic resolution at Mn-Kα and 1 keps 126 eV is used.

X-ray structural method (XRD). It was used for determining the phase composition of phosphate coatings. The investigations were carried out by TUR-M-62 diffractometer with focusing system Bragg-Brentano, using Co-Kα (1.79021 Å), with interval 5° < Θ < 55°.

3. Results and discussions

Table 1 shows the values of the main indicators concerning the concentrates for phosphating: ρ – density; pH; σ – conductivity; K_o – total and K_c – free acidity.

Table 1. Main characteristics of the phosphating concentrates.

Solutions	ρ , g/cm ³	pH	σ , mS/cm	K_o	K_c
ZnPh	1.290	0.79	98.9	300	32
MnPh	1.305	0.51	118.9	334	70

3.1. Gravimetric investigations

The gravimetric method was used to elucidate the effect of the operating conditions (concentration and temperature of the phosphating solutions as well the duration of the process) on the coating thickness M_1 . Figure 1 shows typical relationships thickness/mass of phosphate coatings, M_1 – time, min obtained at optimal conditions (the surfaces of the treated steel samples are coated by homogenous dense films): 80°C temperature, different working concentration and duration of the process.

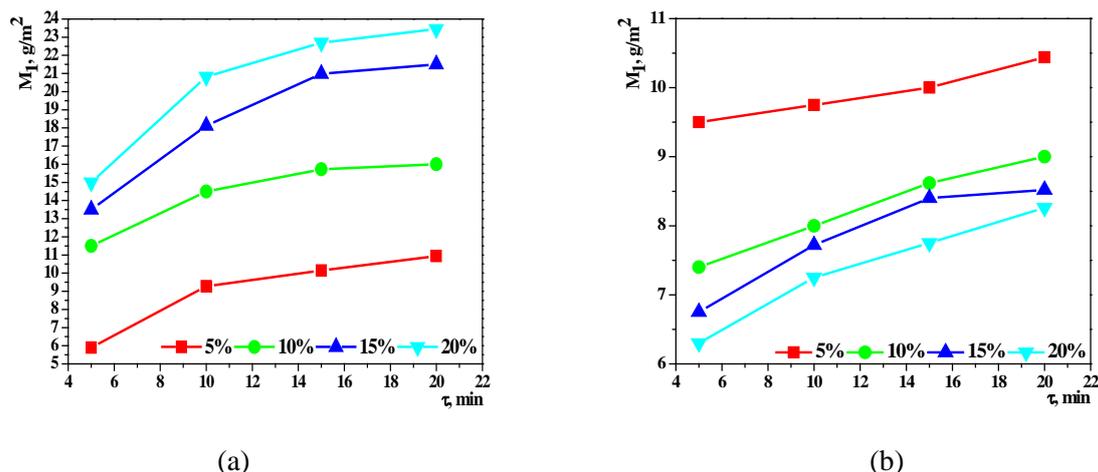


Figure 1. Effect of the phosphating duration, τ , min on the thickness/mass of the phosphate coatings obtained in the phosphating solutions, M_1 , g m⁻²: (a) ZnPh; (b) MnPh.

It is obvious that with increase of the solution concentrations in the range of 5 ÷ 20 % vol for both phosphating concentrates the mass/thickness of the phosphate films increases. The results show also, that the thicknesses of the coatings obtained in ZnPh solutions are significantly higher.

3.2. Electrode potentials measurement

The corrosion resistance of the phosphate coatings was determined in model aqueous solutions of 0.6NaCl. The tests itself includes an immerse procedure for about 1 h of two samples in the NaCl solution. The coating was determined as resistant if for 1 h (an empirically chosen time interval) no changes in the surface as colour spots or colorization of the solutions occur. Meanwhile, in parallel to these tests the corrosion potential of the samples were measured that allowed to compare the behaviour with that of uncoated steel samples.

The potential behaviour shown in Figure 2 is relevant to the corrosion resistance of phosphate coatings in 0.6 M aqueous solutions of NaCl. The plots reveal that just after the sample immerse in the corrosion medium the potentials shift sharply in the negative directions and after a certain

accommodation time interval (about 500 seconds) a stable state is attained. The corrosion potential of an uncoated steel sample is more negative than the phosphate coated ones.

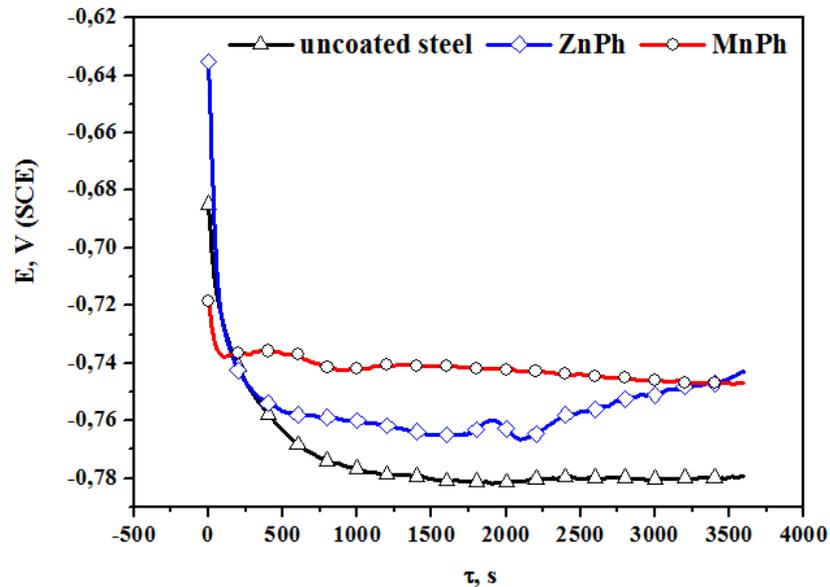


Figure 2. Relationships potential-time in 0.6 M NaCl (open circuit): 20 % wt.; 80°C; 15 min.

3.3. Potentiodynamic polarization investigations

The potentiodynamic polarization studies of the phosphate coatings were carried out at room temperature (20°C) in model aqueous solutions of 0.6 M NaCl. The scanning rate of 10 mV s⁻¹ was chosen based on preliminary test runs. The target of these experiments was to obtain information about the corrosion resistance of the phosphate coatings formed in the corresponding model media in course of their cathodic and anodic polarization and consequently to compare them.

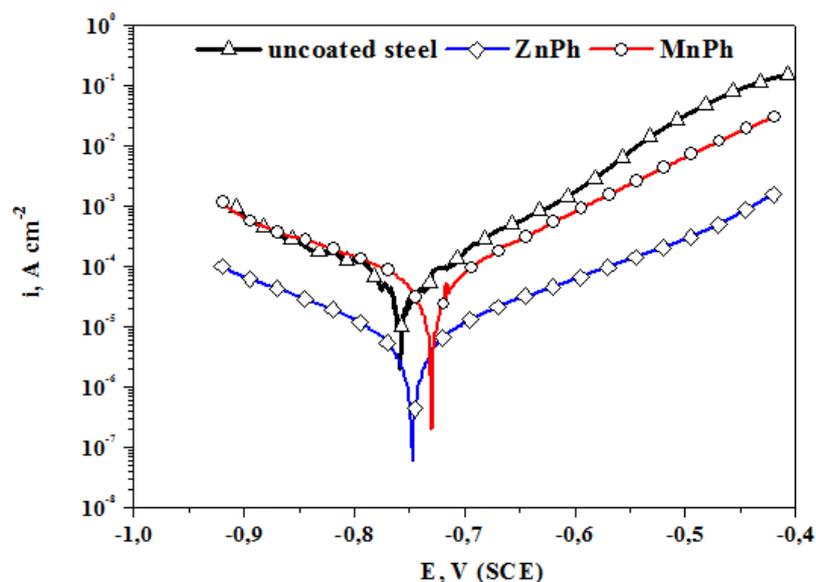


Figure 3. Potentiodynamic polarization relationships of the phosphate coatings in 0.6 M NaCl: 20 % wt.; 80°C; 15 min.

The potentiodynamic polarization relationships of the phosphate coatings (see Figure 3) obtained in the model solutions of 0.6 NaCl allow estimating both the corrosion potentials and the corresponding currents, summarized in Table 2. The potential of the coating, obtain in the MnPh solution is 30 mV more positive and the potential of the coating, obtain in the ZnPh solution is 15 mV more positive then the potential of the uncoated steel. In spite of these little differences, the more positive potentials and the low values of the coated samples show better corrosion resistance vs. uncoated steel surface.

Table 2. Corrosion parameters of the coatings in 0.6 M NaCl.

Model solution	ZnPh solution		MnPh solution		Uncoated steel	
	E_{corr} V (SCE)	i_{corr} A cm ⁻²	E_{corr} V (SCE)	i_{corr} A cm ⁻²	E_{corr} V (SCE)	i_{corr} A cm ⁻²
0.6 M NaCl	-0.745	1.1x10 ⁻⁶	-0.730	8.0x10 ⁻⁶	-0.760	2.0x10 ⁻⁵

3.4. Optical microscopy

The micrographic pictures on Figure 4 demonstrates surface of the phosphate coatings obtain into ZnPh and MnPh solutions at 20 % wt.; 80°C and 15 min duration time. Surfaces of the coatings are homogeneous with dense fine film crystals of dark grey and black colour. The crystals in ZnPh coating are bigger, with comparison to these in MnPh coating.

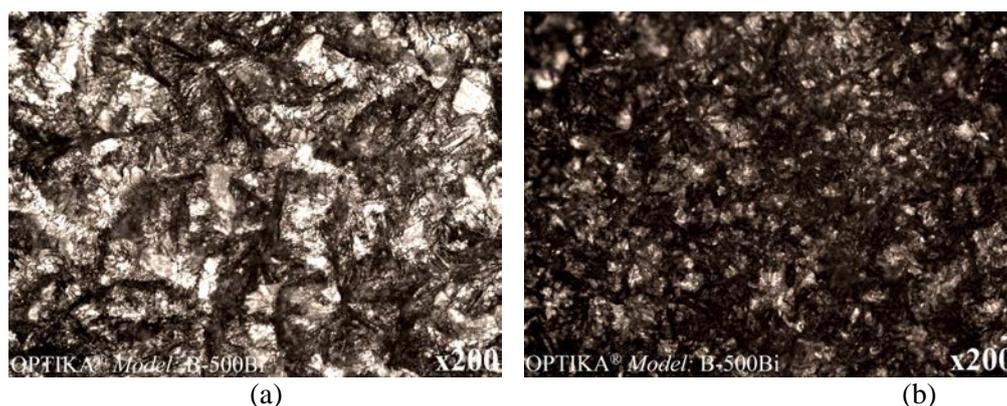


Figure 4. Optical microscopy of the phosphate coatings: (a) ZnPh solution; (b) MnPh solution.

3.5. SEM and EDX analyses

The microphotographs in Figure 5 and Figure 6 demonstrate the morphology of the phosphate coatings obtained on steel surfaces into phosphating solutions. It follows from the figures that the habit of coatings is constant – i.e. the crystals initiate from one centre and increase radially (like spherulite). Crystals have length between 5 and 50 μm.

Table 3. EDX analyses of the elements in the coatings.

Elements	ZnPh solution		MnPh solution	
	Weight %	Atomic %	Weight %	Atomic %
<i>O</i>	26.26	53.97	19.11	43.26
<i>Zn</i>	44.00	22.13	29.05	16.09
<i>P</i>	13.53	14.36	13.45	15.73
<i>Fe</i>	16.21	9.55	36.43	23.63
<i>Mn</i>	–	–	1.97	1.30

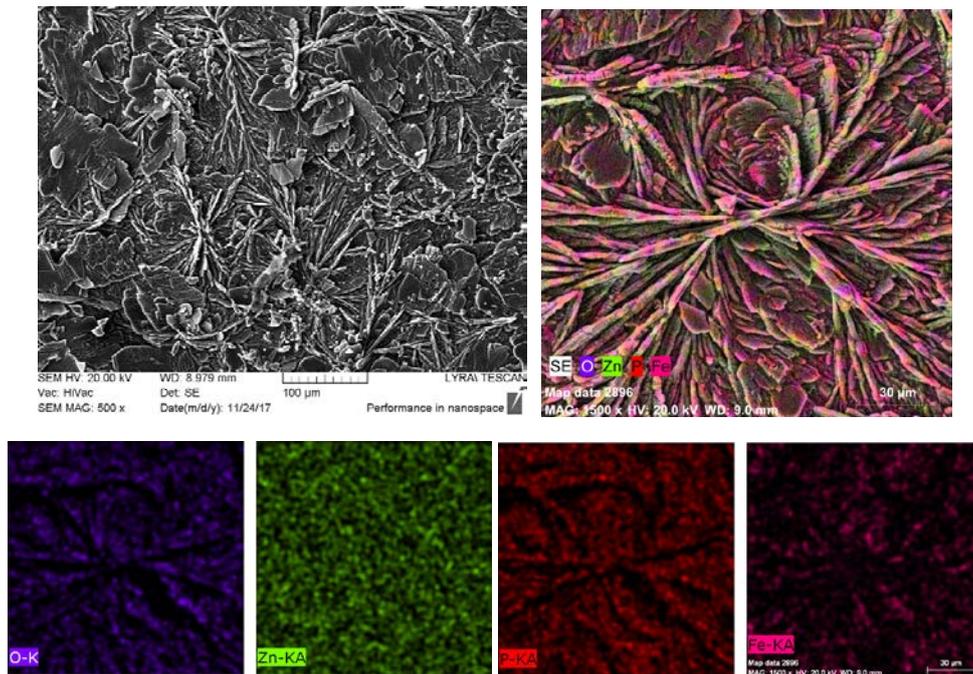


Figure 5. SEM – microphotograph and distribution of the elements in the coating obtained in ZnPh solution.

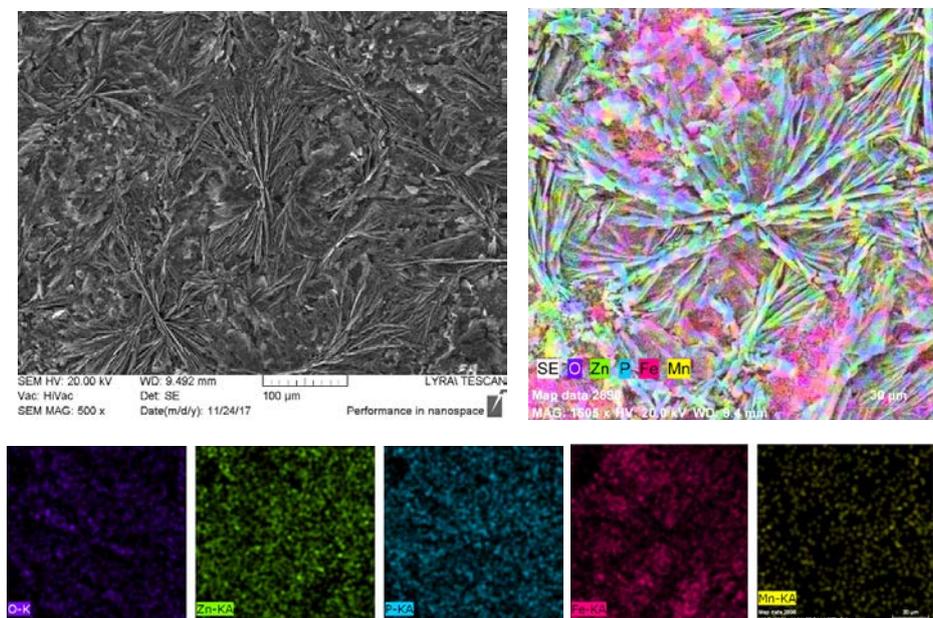


Figure 6. SEM – microphotograph and distribution of the elements in the coating obtained in MnPh solution.

The surfaces in different colours illustrate the distribution of the elements containing in the coating.

The EDX-analysis is performed on specimens treated in phosphate solutions: 20 % wt.; 80°C and 15 min. The basic elements containing in the coatings determined by means of this analysis are O, Zn, P, Fe and a quantity of Mn in the coating produced in MnPh solution. The results of EDX-analysis are presented in Table 3.

3.6. X-ray structural method

The XRD-spectra of the crystalline coatings grown in the ZnPh and MnPh phosphating solutions are shown in Figure 7.

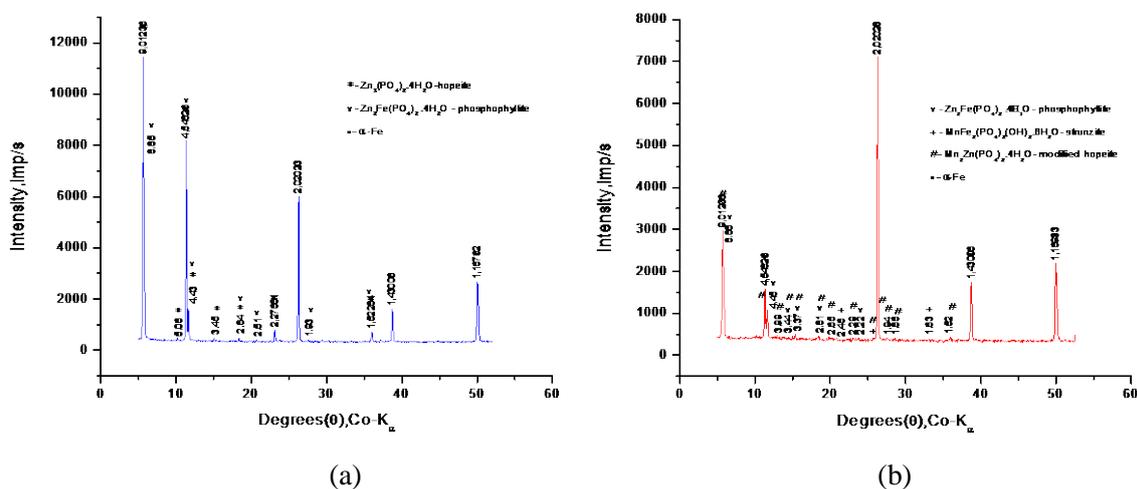


Figure 7. XRD-spectra of the crystalline phosphate coatings grown in: (a) ZnPh; (b) MnPh.

The XRD analysis principally indicates presence of hopeite; phosphophyllite, quasihopeite, strunzite and mixtures of them in the coatings obtain in two phosphating solutions.

4. Conclusions

With the help of chemical, electrochemical and physical-analytical methods the processes of heavy crystal phosphating of carbon steels have been investigated. The properties of the coatings produced in ZnPh and MnPh solutions were determinate.

The addition of manganese phosphates to the ZnPh solution leads to increase the conductivity, decrease the pH value and to increase the value of it's free acidity. With increase of the solution concentrations in the range of 5 ÷ 20 % vol. for both phosphating concentrates the mass/thickness of the phosphate films increases. The results show also, that the thickness of the coatings obtained in ZnPh solutions is significantly higher.

The electrode potential during the formation of the coatings was more positive when in the phosphating solution there're manganese phosphates. In the media of 0.6 M NaCl electrode potential of the coating produced in MnPh solution is again more positive than the other. The potentiodynamic polarization relationships of the phosphate coatings, the more positive potentials and the low values of the coated samples show better corrosion resistance vs. uncoated steel surface.

Surfaces of the coatings are homogeneous with dense fine film crystals of dark grey and black colour. The crystals in ZnPh coating are bigger, with comparison to these in MnPh coating.

The XRD analysis principally indicates presence of hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] and phosphophyllite [$Zn_2Fe(PO_4)_2 \cdot 4H_2O$] in the coating obtain in the ZnPh solution. And in the coating produced in the other MnPh solution there is a presence of quasihopeite [$Mn_2Zn(PO_4)_2 \cdot 4H_2O$], strunzite [$MnFe_2(PO_4)_2(OH)_2 \cdot 6H_2O$] and phosphophyllite [$Zn_2Fe(PO_4)_2 \cdot 4H_2O$].

5. References

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