Mössbauer Spectroscopy from Magnetic Nanoarchitectures to Environmental Science: A Symposium in Honor of Dr. Jean-Marc Greneche
American Chemical Society (ACS Fall 2021), 22-26 August 2021, Atlanta, GA, USA and online (hybrid event)

EFFECTS OF Cr^{3+} IONS AND HEXAMETHYLENETETRAMINE ON THE FORCED HYDROLYSIS OF $FeCl_3$ SOLUTIONS

Marko Robić[1], Mira Ristić[1], Stjepko Krehula[1], Erno Kuzmann[2], Zoltan Homonnay[2], Svetozar Musić[1]
1-*Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia*
2-Eotvos Lorand Tudomanyegyetem, Budapest, Hungary
Marko.Robic@irb.hr

Introduction

The most simple way to precipitate iron oxides is slow or forced hydrolysis of Fe(III) salt solutions. These precipitation processes are influenced by various addings which can change or pronounce some specific properties of iron oxides. In this work HMTA (hexamethylenetetramine) was used in order to extend the pH region of the homogeneous Fe^{3+} hydrolysis, as well as to eliminate the problems that can occur with abrupt addition of NaOH or NH_4OH solution to the system (heterogeneous precipitation). On the other hand, using HMTA as adding in Fe-Cr system allowed doping with chromium, since Cr^{3+} ions don't form hydroxyl complexes up to pH~4. Then, with further pH increase, there is abrupt hydrolysis of Cr^{3+} ions [1].

In this work, the phase analysis and nano/microstructural properties of the precipitates formed by forced hydrolysis at 160°C of $FeCl_3$ solutions in the presence of Cr^{3+} ions and HMTA were investigated. Due to the complexity of these precipitation systems the phase compositions were determined by combining X-ray diffraction, ^{57}Fe Mössbauer and FT-IR spectroscopy, whereas nano/microstructural properties were analysed with scanning electron microscopy (FE SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). 2-XRD lines ferrihydrite, α-FeOOH and β-FeOOH obtained in described systematic study were the precursors of α-Fe_2O_3 as the end-product. The present investigation is not important only from the academic standpoint. It is also important for better understanding of different processes, such as aqueous and atmospheric corrosion of steel, catalysis and photocatalysis, role of Cr-doped electrode material for Li-ion batteries or decontamination of Cr-polluted waters with iron oxides.

Results

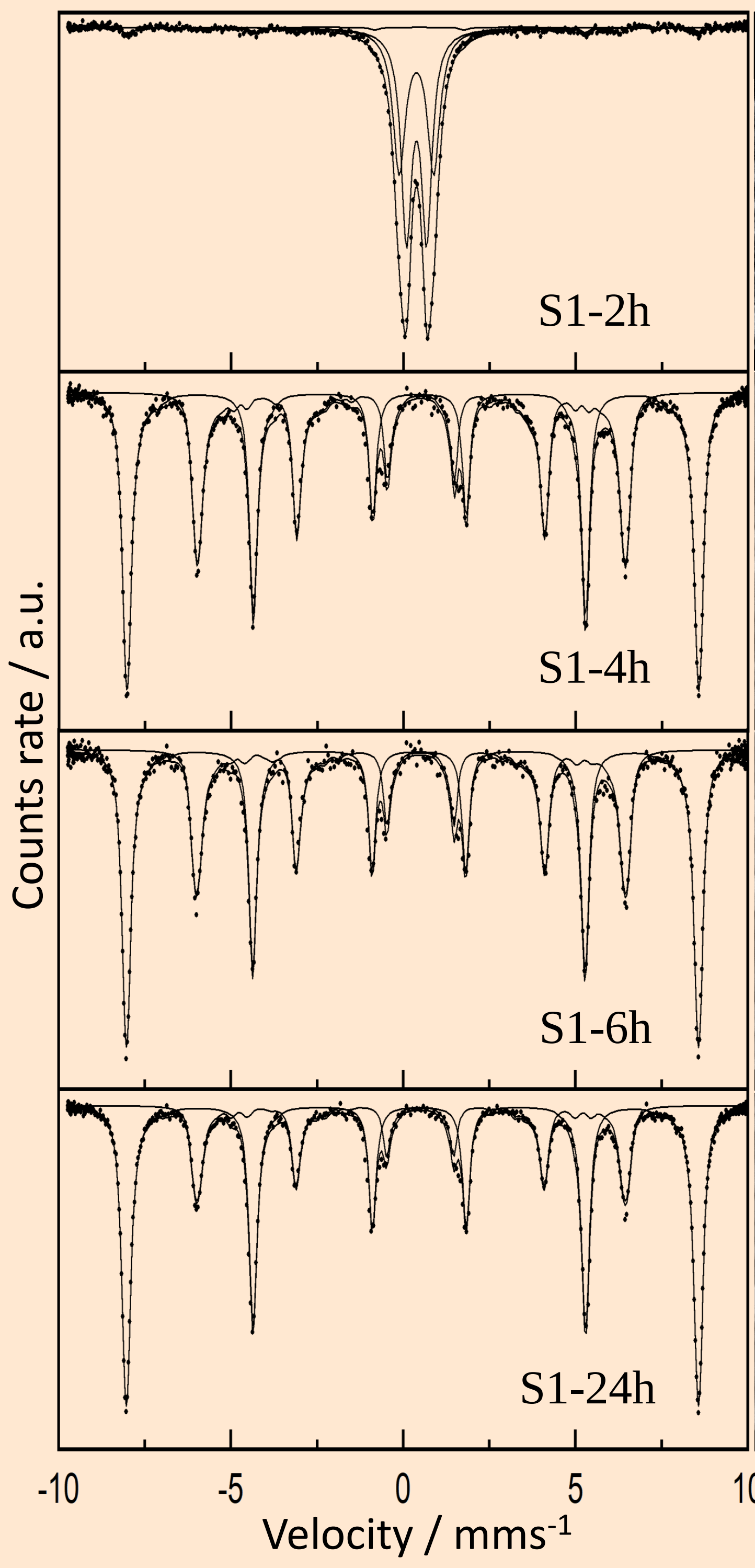


Fig. 1. ^{57}Fe Mössbauer spectra of S1 series recorded at 20°C.

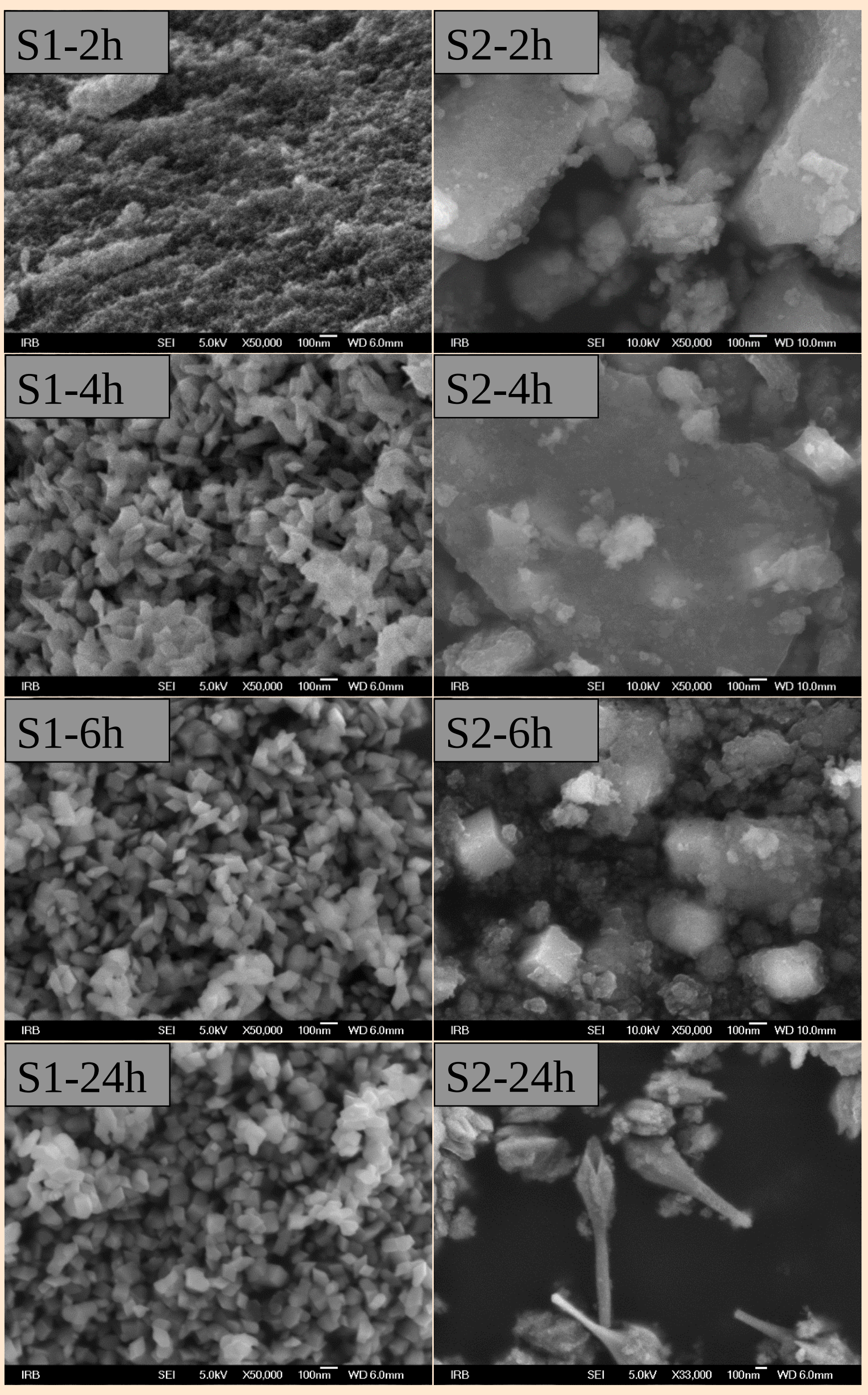


Fig. 2. FE SEM images of S1 and S2 series.

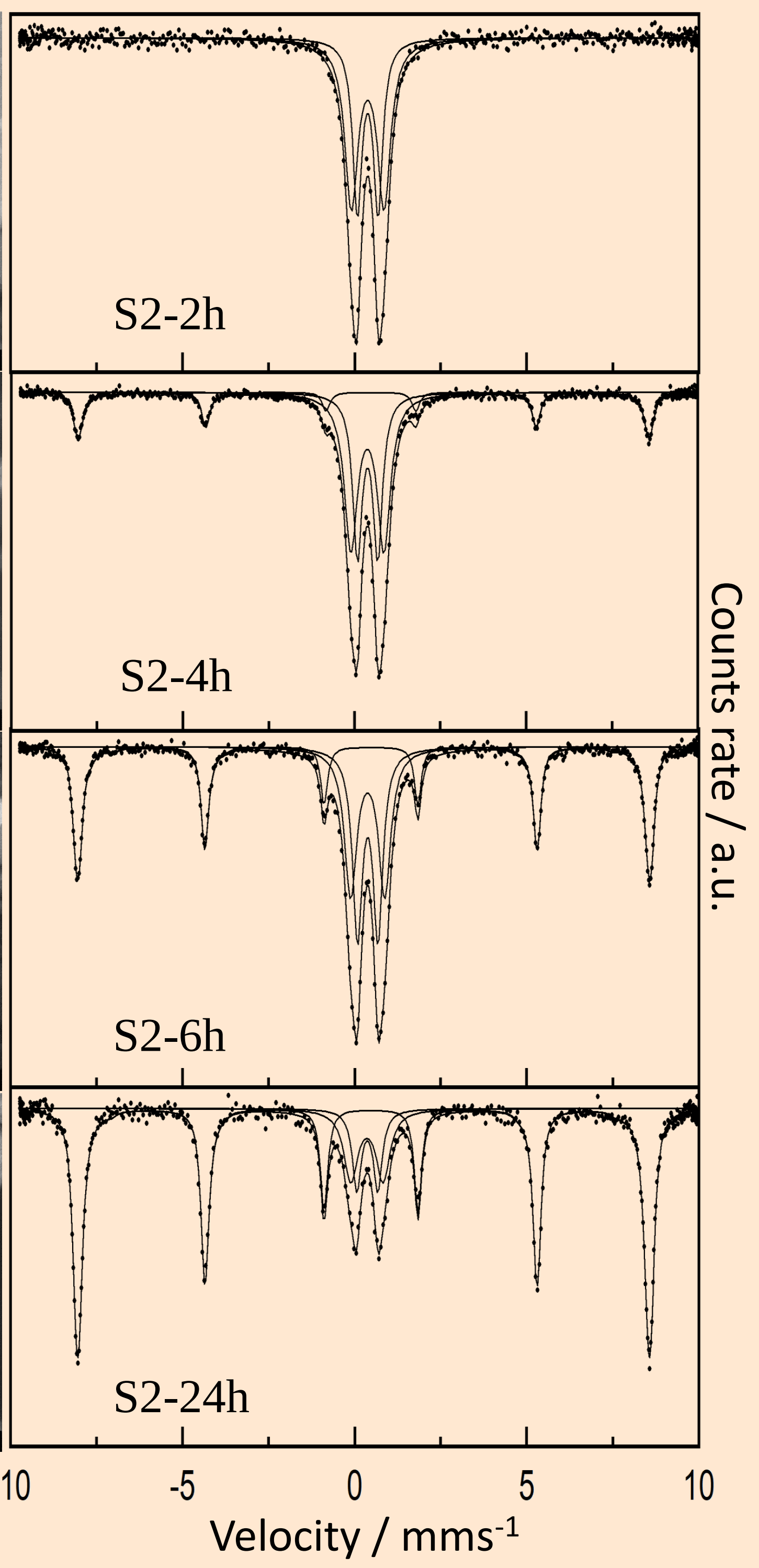
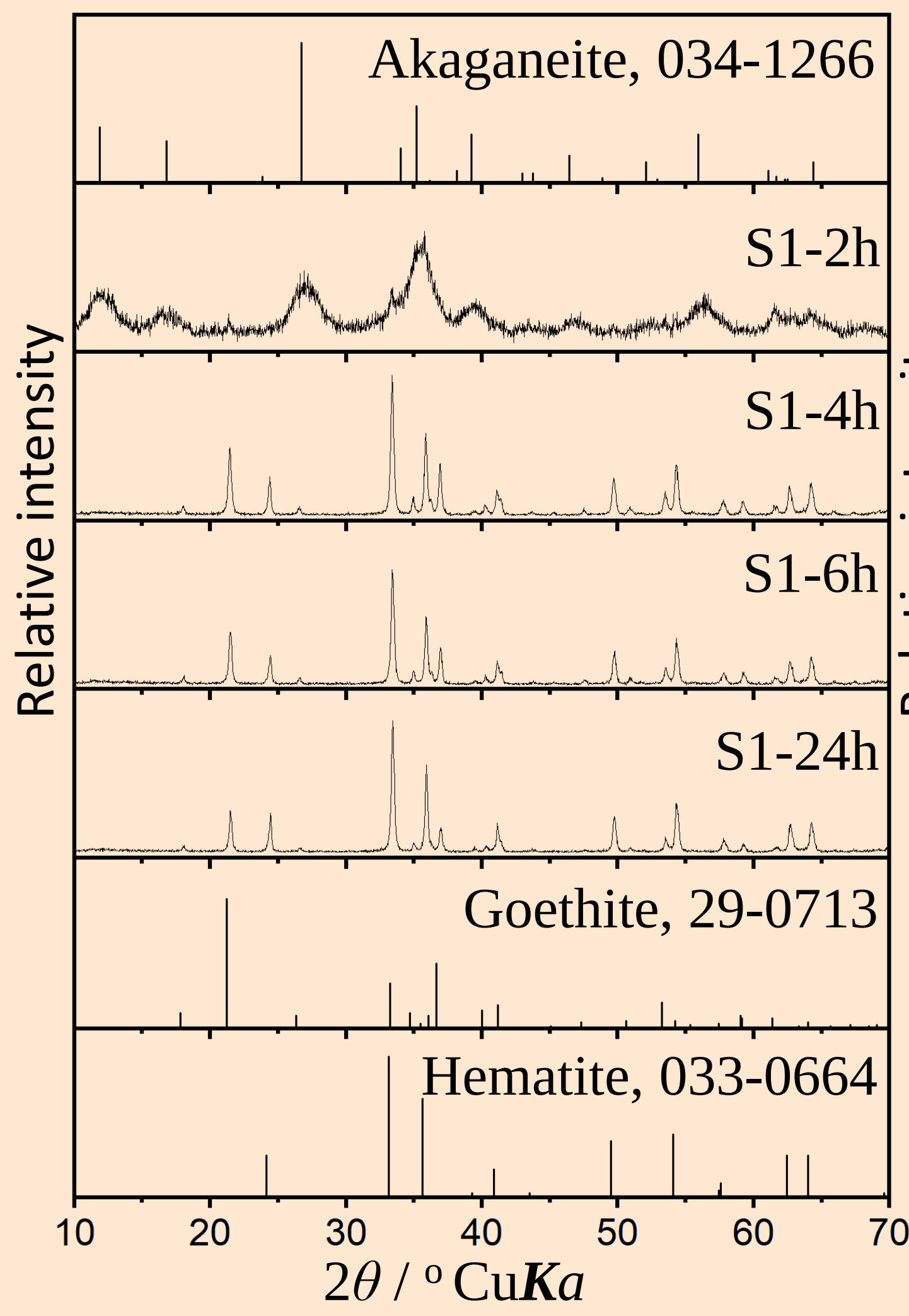


Fig. 3. ^{57}Fe Mössbauer spectra of S2 series recorded at 20°C.



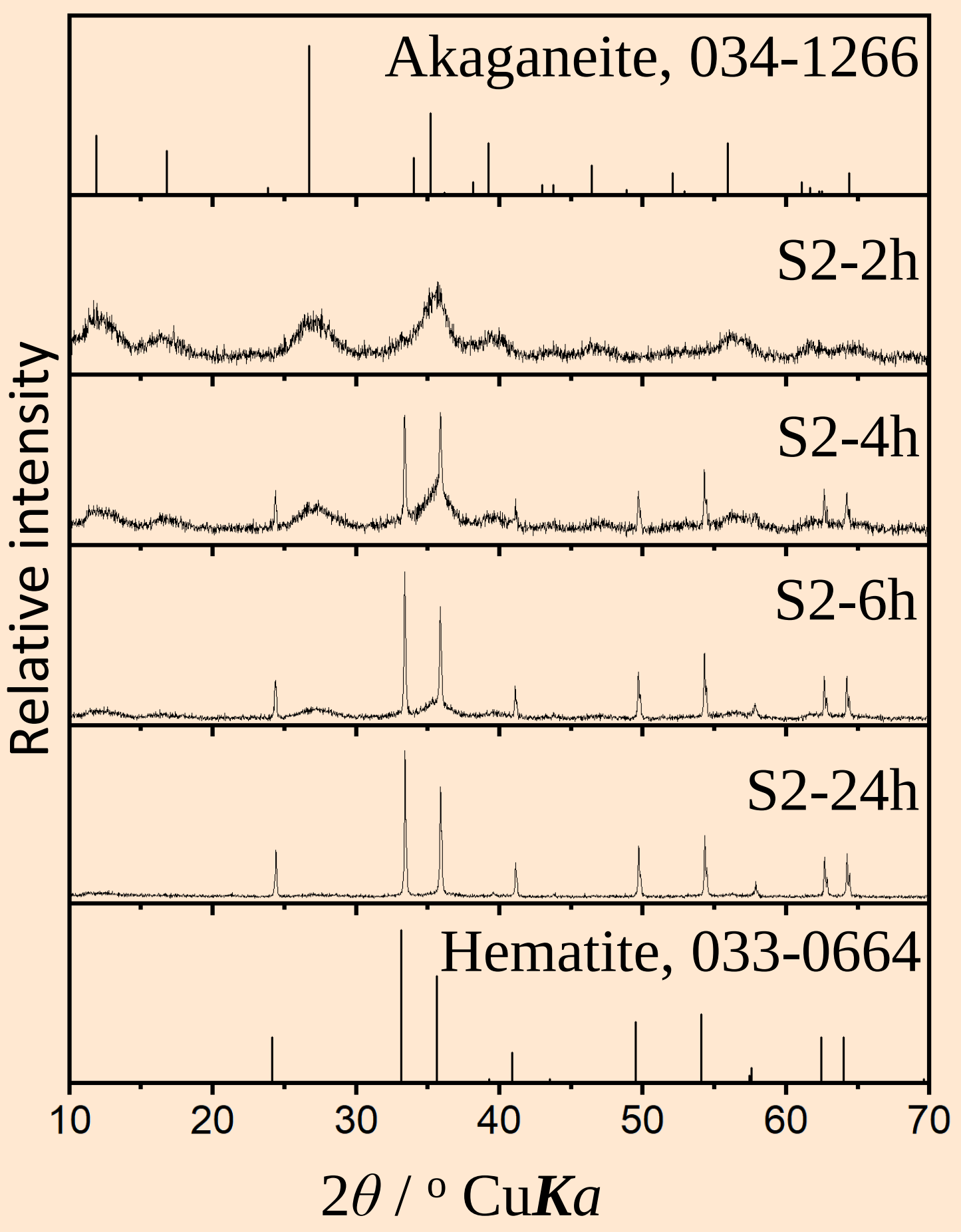


Fig. 4. (left and above) XRPD patterns of S1 and S2 series.

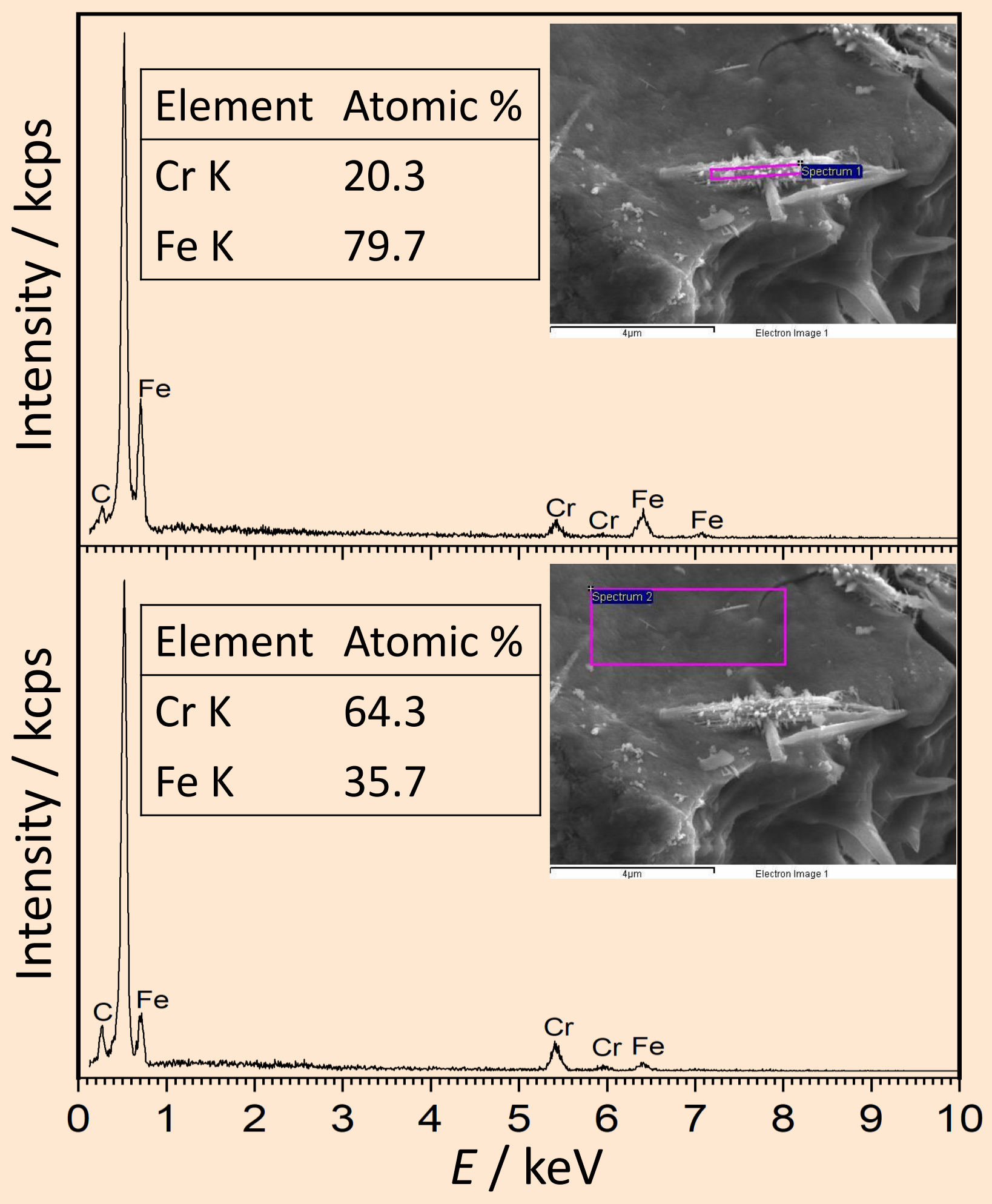


Fig. 5. EDS spectra of sample S3-24h.

Experimental

Forced hydrolysis
teflon-lined pressure vessels
gravity oven (160°C)

Washing
high-speed centrifuge

Drying
laboratory dryer
24 h (90-110°C)

Cation salts: $FeCl_3 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$
Adding: HMTA (*Urotropine*)
Solvent: miliQ water

HMTA undergoes homogeneous hydrolysis in the water medium at elevated temperature in line with chemical reactions:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

Sample	Cr / %	$FeCl_3$ / M	$CrCl_3$ / M	pH_{start}	pH_{final}
S1-2h	0	0.20	Ø	2.10	5.23
S1-4h	0	0.20	Ø	2.10	7.48
S1-6h	0	0.20	Ø	2.10	8.08
S1-24h	0	0.20	Ø	2.10	7.82
S2-2h	10	0.18	0.02	1.99	5.33
S2-4h	10	0.18	0.02	1.99	7.30
S2-6h	10	0.18	0.02	1.99	7.20
S2-24h	10	0.18	0.02	1.99	8.03
S3-24h	50	0.01	0.01	5.44	9.77

Table 1. (left) Experimental conditions for sample synthesis. All samples were autoclaved with 0.25 M HMTA (starting solution) at 160°C.

Table 2. ^{57}Fe Mössbauer parameters of selected samples recorded at 20°C.

Sample	Line	δ / mm s^{-1}	$\mathit{\Delta}$ or E_q /mm s^{-1}	B_{hf} / T	$\mathit{\Gamma}$ / mm s^{-1}	Area /%	Phase
S1-2h	M	0.37 (f)	-0.20 (f)	51.40	0.31	3.50	H
	Q_1	0.38	0.59		0.36	52.50	A
	Q_2	0.38	1.00		0.44	44.00	A
S1-4h	M_1*	0.37	-0.19	51.32	0.24	57.19	H
	M_2*	0.37	-0.28	36.57	0.22	42.81	G
S1-6h	M_1*	0.37	-0.19	51.40	0.24	60.42	H
	M_2*	0.37	-0.27	36.96	0.22	39.58	G
S1-24h	M_1*	0.37	-0.20	51.39	0.24	69.84	H
	M_2*	0.36	-0.26	36.75	0.22	30.16	G
S2-2h	Q_1	0.38	0.60		0.32	41.98	A
	Q_2	0.38	0.95		0.46	58.02	A
S2-4h	M*	0.37	-0.21	51.30	0.24	19.47	H
	Q_1	0.38	0.59		0.33	34.35	A
	Q_2	0.37	0.96		0.46	46.19	A
S2-6h	M*	0.37	-0.21	51.41	0.22	39.47	H
	Q_1	0.38	0.60		0.36	30.23	A
	Q_2	0.38	0.99		0.43	30.30	A
S2-24h	M*	0.37	-0.22	51.47	0.24	72.36	H
	Q_1	0.37	0.61		0.30	11.54	A
	Q_2	0.36	0.94		0.48	16.10	A
S3-24h	M_1*	0.37	-0.21	50.88	0.26	17.50	H
	M_2	0.37 (f)	-0.26 (f)	34.56	0.50 (f)	6.90	G
	Q**	0.34	0.85		0.35	75.60	FH

Key: δ=isomeric shift relative to α-Fe at 20°C, B_{hf} =hyperfine magnetic field, $\mathit{\Delta}$ or E_q=quadrupole splitting, $\mathit{\Gamma}$=linewidth, M=sextet, Q=quadrupole doublet, H=hematite, G=goethite, FH=ferrihydrite, A=akaganeite, (f)=fixed parameters in fitting process.

Remark: Mössbauer spectra were fitted using the distribution of B_{hf} (*) or $\mathit{\Delta}$ (**)

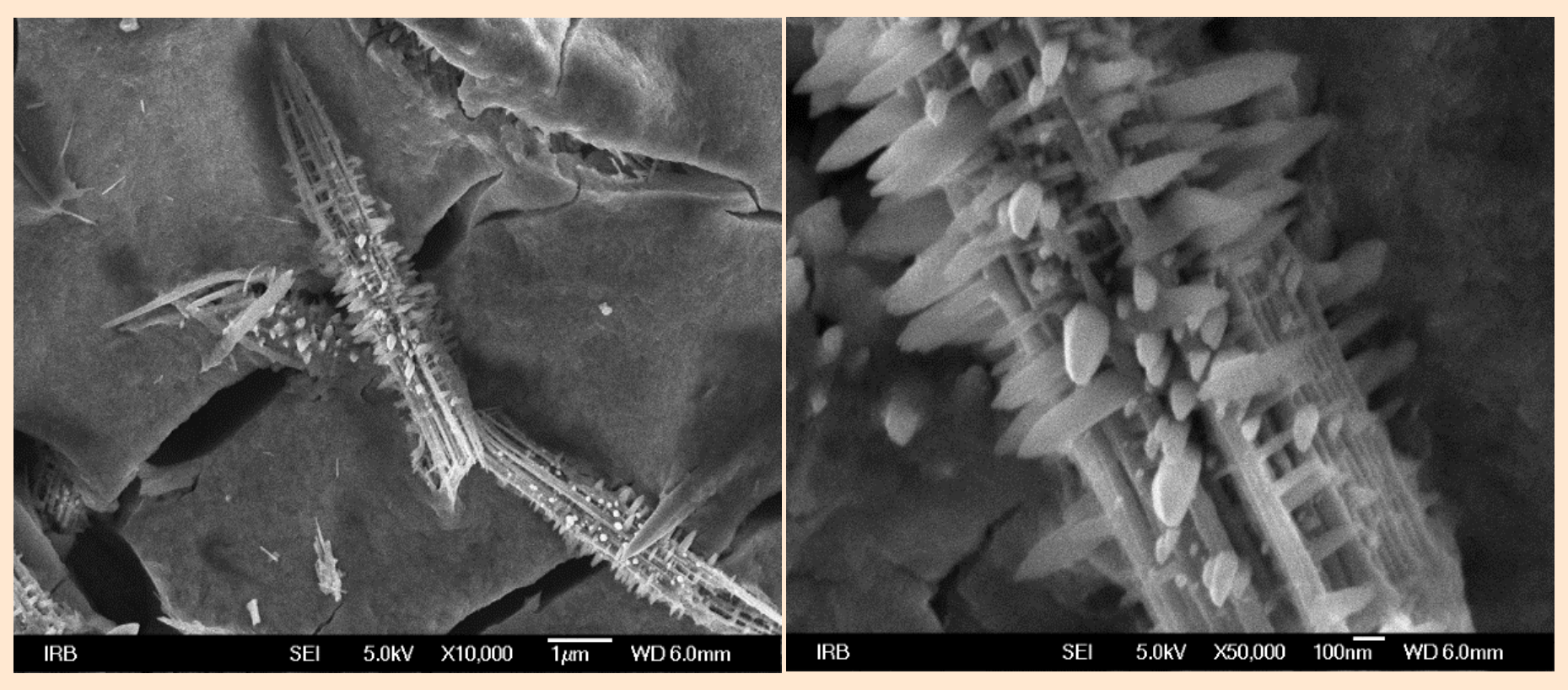


Fig. 6. FE SEM images of sample S3-24h (dendritic nano/microstructures).

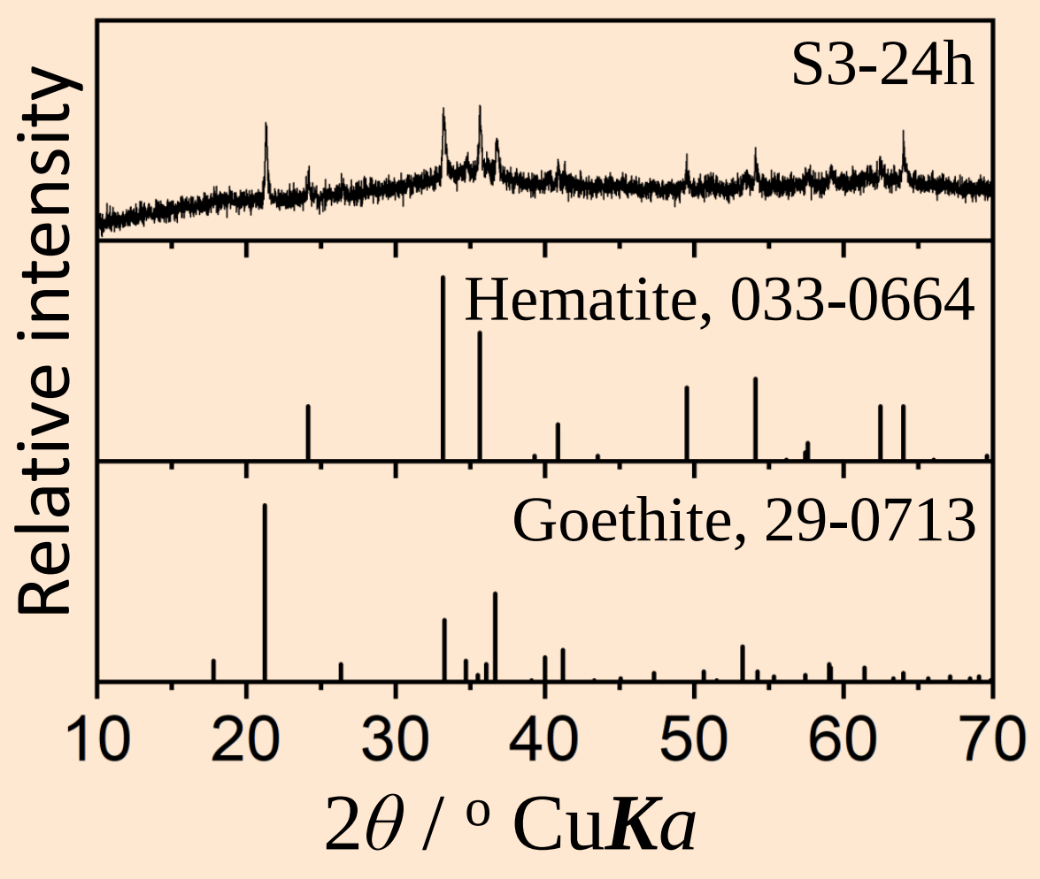


Fig. 7. XRPD pattern of sample S3-24h.

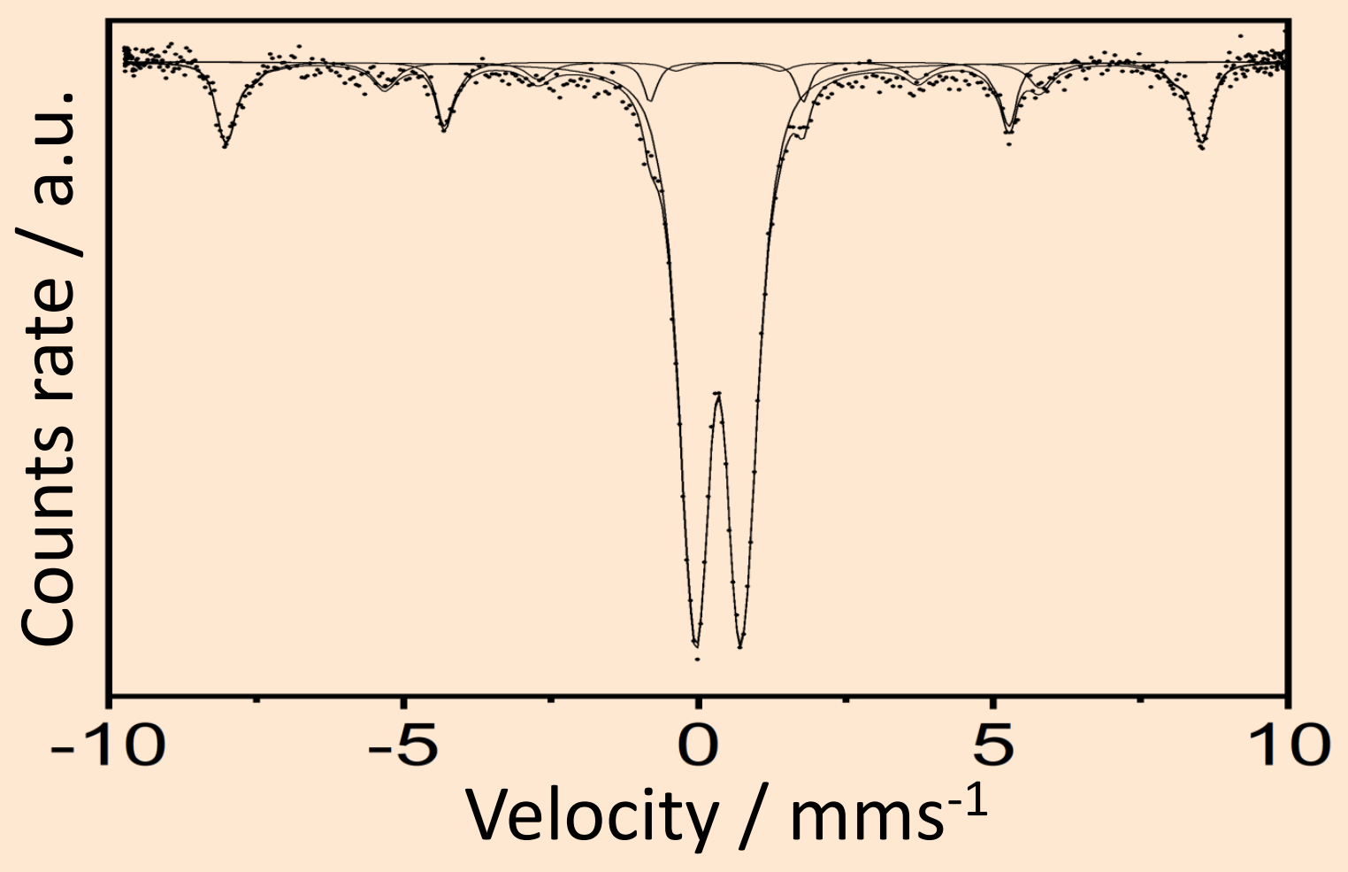


Fig. 8. ^{57}Fe Mössbauer spectra of S3-24h recorded at 20°C.

Conclusions

- Homogeneous hydrolysis of HMTA in all precipitation systems resulted in pH increase. This effect had a strong influence on the phase composition and particle shape.
- New particle shapes were obtained. Onion-like particle shape was obtained in synthesis with 10% Cr^{3+}, while dendritic nano/microstructure (composite) was obtained in synthesis with 50% Cr^{3+}.
- Decreased HMF values of α-FeOOH and α-Fe_2O_3 phases (sample S3-24h) indicate the formation of solid solutions which can be assumed due to very similar ionic radii of Fe^{3+} and Cr^{3+} [2].
- XRPD and EDS analysis of sample S3-24 (made with 50% Cr^{3+}) also support the formation of solid solutions. EDS analysis showed the amorphous-like area is rich in chromium (64%), whereas the dendrite area is rich in iron (~80%).

References

[1] S. Musić, J Radioanal. Nucl. Chem. 100 (1986) 185-196.
[2] R. D. Shannon, Acta Cryst A 32 (1976) 751-767.

Acknowledgement

This work is financially supported by Croatian Science Foundation (HRZZ), project number IP-2016-06-8254.