

Spremenjeno kristaljenje vodnega kamna pri magnetni obdelavi vode

Modified Scale Crystallization in Magnetic Water Treatment

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Magnetna obdelava vode (MOV) je alternativna metoda priprave napajalnih vod za nadzor vodnega kamna in prav tako postaja pomembna pri izboljšavah drugih tekočin, ki vsebujejo vodo. Govor je o učinkih naprav MOV, med njimi o spremenjenem kristaljenju vodnega kamna in spremenjeni stabilnosti vodnih disperzij s poudarkom na spremenjeni hidrataciji ionov in trdnih površin zaradi magnetne protonske resonance kot enega izmed možnih mehanizmov. Nadalje je predlagana pojasnitev pospešenega obarjanja aragonita.

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(Ključne besede: priprava vode, kristaljenje CaCO₃, hidratacija ionska, magnetohidrodinamika)

Magnetic water treatment (MWT) is an alternative method of supplied-water conditioning for scale control and is also important in the amelioration of other water-based fluids. The effects of MWT devices, such as the modified crystallization of the scale-forming components and modified stability of the dispersion are discussed with the emphasis on the modified hydration of ions and solid surfaces due to magnetic proton resonance as one of the possible mechanisms. In addition, a possible explanation for the accelerated aragonite precipitation is proposed.

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0 UVOD

Nastajanje oblog vodnega kamna je pogosta in draga težava v mnogih industrijskih procesih, ki so napajani z naravnimi vodami. Do oblog na stenah naprav pride zaradi naravne prenasičenosti napajalne vode ali zaradi prenasičenja, ki se vzpostavi med ogrevanjem vode, padcem tlaka ali dvigom pH med samo obdelavo vode. Trde obloge zmanjšujejo pretočne zmogljivosti, povečujejo porabo električne energije črpalk in zahtevajo periodično čiščenje.

MOV igra vse pomembnejšo vlogo alternativne metode pri pripravah industrijskih vod. Njene prednosti v primerjavi z znanimi kemijskimi metodami mehčanja vode so: nizki investicijski in obratovalni stroški, preprosta vgradnja, ohranjanje kakovosti vode (npr. organoleptičnih lastnosti) in prispevek k varstvu okolja.

Pri napravah MOV, ki so bile dobro načrtovane za določen vodovodni sistem in dano sestavo vode [1], lahko pričakujemo veliko učinkovitost pri preprečevanju nastanka trdnih oblog vodnega kamna, še posebej v ogrevanih in cirkuliranih vodovodnih sistemih.

0 INTRODUCTION

The build up of scale deposit is a common and costly problem in many industrial processes which use natural water supplies. Deposits on the equipment walls result from the natural oversaturation of the supplied water or oversaturation caused by water heating, pressure drop or a pH increase during the water processing. The hard-scale deposit reduces water flow capacities, increases the electrical power consumption of pumps and reduces the heat exchanging capabilities of heated surfaces leading to higher operating costs and need to a periodically remove the scale.

MWT is becoming increasingly important as an alternative method of industrial water conditioning. Low investment and operating costs, easy installation, water quality (i.e. organoleptic properties) and ecological benefits are some of the advantages over the well-known chemical methods used for water softening.

MWT devices which are well designed for a particular water composition and industrial process [1], are very effective in preventing hard-scale formation, especially in heated- and circulated-water systems.

Prvi patent tovrstnih naprav je bil vknjižen v Belgiji leta 1945. Praktične izkušnje s to pionirsko napravo so dale zelo različne rezultate: od izjemne učinkovitosti, do popolne neuspešnosti [2]. Od leta 1960 so bili v nekdanji Sovjetski zvezi za nadzor vodnega kamna z veliko ekonomsko koristjo uporabljani močni elektromagneti [3], v USA pa so bile naprave MOV širše sprejete šele po letu 1975 ([4] in [5]).

1 UČINKI NAPRAV MOV NA NARAVNE IN INDUSTRIJSKE VODE

Praktična uporaba naprav MOV je vse bolj razširjena na področju priprave vod za odstranjevanje ali preprečevanje vodnega kamna, prodira pa tudi na nova področja, to so obdelava cementa in goriva ([6] do [12]). V vseh teh primerih gre za obdelavo tekočine, ki vsebuje določen delež vode, da bi se izboljšale njene biokemijske ali fizikalno-kemijske lastnosti.

Iz magnetno obdelane vode se vodni kamen tvorne komponente (predvsem CaCO_3 v nizko-temperaturnih sistemih in CaSO_4 v pregrevanih sistemih) namesto v obliki težko odstranljivih oblog obarja v suspendirani obliki. Kristali so drugačni po svoji obliki, velikosti in strukturi in so manj adhezivni. V primeru CaCO_3 je bilo opaženo, da se lahko z magnetno obdelavo razmerje aragonit/kalcit bistveno zviša ([13] in [14]). Aragonit je kinetično ugodnejša kristalna faza, ki vsebuje slabo adhezivne kristale igličaste oblike. Kalcit je termodinamično ugodnejša kristalna faza, sestavljena iz rombičnih kristalov, ki lahko zaradi svoje velike adhezivnosti tvorijo trde, težko odstranljive obloge.

Zvišano razmerje aragonit/kalcit delno pojasni obarjanje prašnatih oblog iz magnetno obdelane vode. Čeprav je kristaljenje iz magnetno obdelane vode zelo odvisno od same sestave vode in obratovalnih razmer, je v večini primerov opaženo obarjanje zmanjšanega števila kristalov CaCO_3 , ki so večji in imajo zvišan delež aragonita. Celo kristaljenje iz prenasičene mešanice statično magnetno obdelanih raztopin Na_2CO_3 in CaCl_2 v dobro nadziranih laboratorijskih razmerah je dalo podobne rezultate [15].

2 MEHANIZMI DELOVANJA NAPRAV MOV NA PROCESIRANO VODO

Večdesetletne izkušnje na področju MOV so dale nekaj empiričnih osnov za načrtovanje magnetnih naprav, vendar pa še vedno ostaja odprto vprašanje mehanizem, ki bi natančno pojasnil, kako magnetno polje vpliva na obdelovani vodni sistem. Na temelju številnih eksperimentalnih in teoretskih poročil je sklepati, da mehanizem najverjetneje sestoji iz vzporednih, med seboj prepletenih korakov, ki so odvisni od

The first patent referring to a MWT device was registered in Belgium in 1945. Practical experience with these devices showed very different results: from very effective to completely useless [2]. Since 1960, strong electromagnets have been used in the Soviet Union for scale control in high-temperature water systems with significant economic benefits [3]. In the USA, MWT devices have been accepted since 1975 ([4] and [5]).

1 THE EFFECTS OF MWT DEVICES ON NATURAL AND INDUSTRIAL WATERS

The practical use of MWT devices has become increasingly wide spread for descaling or scale prevention and has penetrated into new fields for other purposes such as biochemistry, medicine, agriculture, dispersion separations, concrete and fuel amelioration ([6] to [12]). In all these cases fluids containing some fraction of water were magnetically treated to improve their biochemical or physicochemical properties.

The scale-forming components (mainly CaCO_3 in low-temperature systems and CaSO_4 in heated systems) precipitate from the magnetically treated water in a suspended form rather than by forming hard-scale linings. The crystals are different in terms of their form, size and structure with lowered adhesivity. For CaCO_3 it was observed that the ratio of aragonite/calcite crystal phases could be increased ([13] and [14]). The former is a kinetically advanced crystal phase of CaCO_3 formed in needle-like crystals which have low adhesion, while the latter is a thermodynamically advanced crystal phase of CaCO_3 formed in rhombic crystals which are able to adhere into compact, hard-to-remove scale.

The increased aragonite/calcite ratio partially explains the precipitation of powder deposits resulting from MWT. Although the crystallization in magnetically treated water is strongly dependent on the water composition and working conditions the precipitation of fewer and larger CaCO_3 crystals with an increased fraction of aragonite was observed in most cases. Even the crystallization in a supersaturated mixture of static magnetically treated solutions of Na_2CO_3 and CaCl_2 under well-controlled laboratory conditions gave similar results [15].

2 MECHANISMS OF MWT – ACTING ON PROCESSING WATER

A long history of practical experiences has provided some empirical bases for designing magnetic devices. However, the mechanism which explains how the magnetic field acts on the treated water still remains uncertain. From the many reports relating to laboratory and theoretical research it can be concluded that the mechanism most probably consists of parallel interacting steps, depending on the construction of the MWT devices, the composition of the supplied water as a

delovnih razmer (npr. hitrosti pretakanja vode in temperature).

V svetovni literaturi je najti dragocene namige, ki poskušajo pojasniti magnetne učinke, vendar nobeden ni dokončno potrjen in tudi ne pojasni vseh učinkov hkrati.

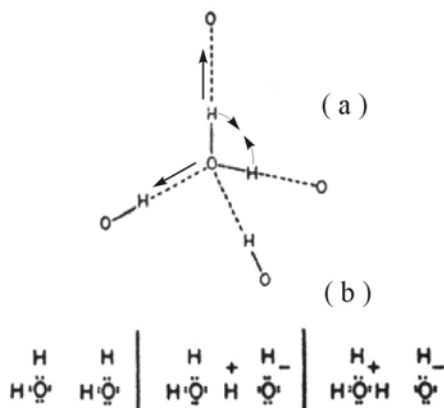
Vodilne hipoteze so:

- magnetno spremenjena hidratacija ionov in trdnih površin
- magnetohidrodinamični učinek na vodne disperzije
- koncentracijski učinki v delovnih kanalih naprav MOV.

Slednji se štejejo kot zvišanje verjetnosti trkov med ioni ali trdnimi delci v določenih območjih delovnih kanalov zaradi turbulence pretakajoče se vode, visoke magnetnosti suspendiranih korozijskih produktov oz. nehomogenosti magnetnega polja naprave [16]. Učinki tega tipa delno pojasnijo agregacijo drobnih že destabiliziranih delcev v večje, medtem ko je spremenjeno kristaljenje in destabilizacijo dispergiranih komponent, ki tvorijo vodni kamen, lažje pojasniti s prvima dvema hipotezama. Kateri mehanizem bo prevladal, je odvisno od sestave vode in samih razmer pri obdelavi. V nadaljevanju bo govor o mogočih vzrokih spremenjenega kristaljenja CaCO_3 .

2.1 Učinek magnetno spremenjene hidratacije na kristaljenje CaCO_3

Eksperimentalna opazovanja vodnih raztopin so med statičnim izpostavljanjem magnetnemu polju pokazala spremembe v nekaterih fizikalno-kemijskih lastnostih, npr.: svetlobni absorbanci [17], viskoznosti [18], topilni entalpiji [19], električni prevodnosti [6], površinski napetosti [20], dielektričnosti [21] in tudi v kristaljenju ter stabilnosti koloidov ([22], [15] in [23]). Opažanja podpirajo hipotezo o magnetno spremenjeni hidrataciji.



Sl.1. Model molekule vode in vodikove vezi [24]
Fig.1. The model of water molecule and hydrogen bond [24]

dispersion/solution system and on the working conditions (i.e. the water flow velocity and temperature).

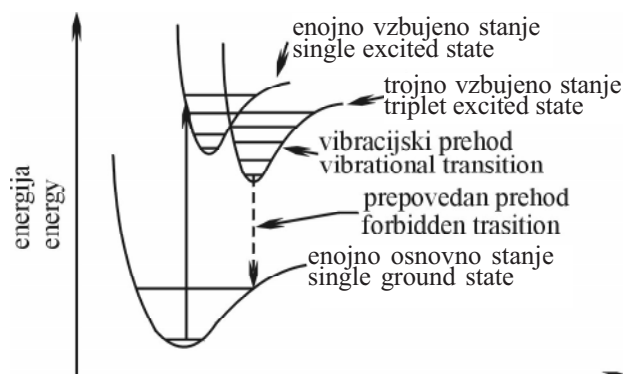
The literature contains some valuable hypotheses explaining magnetic effects on treated water but none is confirmed and none explains all the observed effects simultaneously. The main hypotheses are:

- magnetically modified hydration of ions and solid/solution interfaces;
- magnetohydrodynamic effect on water dispersion systems;
- concentration effects in the working channel of MWT devices.

The concentration effects are considered as an increased probability of particle or ion collisions in particular zones of the working channels due to turbulence of the water flow, easy magnetisation of the suspended corrosion products and the inhomogeneity of the applied magnetic field [16]. Effects of this type partially explain aggregation of fine already-destabilized particles into bigger ones, while modified crystallization and destabilization of dispersed scale-forming components are explained by the first two hypotheses. Which mechanism prevails, depends on the water composition and treatment conditions. A possible explanation for the modified crystallization by magnetically modified hydration will be discussed in the next sections of this paper.

2.1 The effect of magnetically modified hydration on CaCO_3 crystal growth

Experimentally observed changes in the physicochemical habits of water solutions due to static magnetic field exposure, such as light absorbency [17], viscosity [18], solution enthalpy [19], electrical conductivity [6], surface tension [20], dielectricity [21] and modified crystallization and colloid stability ([22], [15] and [23]), support the hypothesis of magnetically modified hydration.



Sl.2. Prehodi spinov [25]
Fig.2. The spin transitions [25]

S statističnega vidika namreč voda sestoji iz prostih molekul in ledu podobnih območij, v katerih so tetraedrično oblikovane molekule vode, med seboj povezane z vodikovo vezjo.

Vodikova vez je delno usmerjena zaradi vodikove resonance med kisikovima atomoma (sl. 1/a). Njena moč je odvisna od oscilacij po veznem kotu in dolžini kovalentnih vezi znotraj molekul vode (sl. 1/b). Te kovalentne oscilacije so odvisne od spinskega stanja protona. Magnetna resonanca dveh sosednjih protonov med magnetno obdelavo lahko povzroči spinski preskok (sl. 2) iz enojnega osnovnega stanja (antivzporedna orientacija spinov) v trojno vzbujeno stanje (vzporedna usmeritev spinov), kar lahko posredno privede do oslabilve vodikove vezi.

Neposredna vrnitev v prvotno stanje je po teoriji kvantne fizike prepovedan prehod. Vrnitev po prvotni poti, ki zahteva aktivacijsko energijo, pojasni magnetni spomin - opaženo trajanje učinka magnetne obdelave še nekaj ur ali celo dni po končani obdelavi. Razpoložljiva energija v praktičnih razmerah statične magnetne obdelave je namreč zanemarljiva v primerjavi s termično energijo atomov oz. molekul, ki se sprošča med atomske spremembe v nanosekundah do milisekundah, če te niso povzročene z znotraj atomskimi spremembami v daljših sprostitvenih časih.

Tako oslabljen mreža vode bi pomenila oslabljeno hidratacijo večine ionov v naravnih vodah (z izjemo K^+ in Cl^-), ionov, ki se raztapljajo z nameščanjem v praznine vodne mreže in jo pri tem dodatno krepijo. Po drugi strani pa bodo nekateri ioni (npr. Fe^{2+}), ki se v naravnih vodah pojavljajo v majhnih koncentracijah in se raztapljajo s tvorbo lastne ovojnice iz prostih molekul vode, postali bolj hidratirani. V skladu s to hipotezo so meritve protonske magnetne resonance potrdile magnetno oslajeno hidratacijo raztopine $Ca(HCO_3)_2$ in ojačano hidratacijo koloidnega železa [26].

Spremembe v hidrataciji delno pojasnijo spremenjeno kristaljenje $CaCO_3$ med končano MOV in po njej. V splošnem kristalna rast poteka skozi več zaporednih korakov, med katerimi najpočasnejši korak določa hitrost rasti kristala. V primeru $CaCO_3$ je bila delna hidratacija kristalotvornih ionov ugotovljena kot najpočasnejši korak [27]. Tako lahko magnetno oslajena hidratacija Ca^{2+} in HCO_3^- vodi v pospešeno kristalno rast $CaCO_3$ in s tem tvorbo večjih kristalov.

3 SKLEP

V mnogih poročilih raziskav s področja MOV ([28] do [31]) je opaziti pomen komponent, ki vsebujejo železo. Nekateri naprave MOV se lahko štejejo zgolj kot žrtvovane anode (katerih raztapljanje se lahko pospeši z delovanjem magnetnega polja),

From the statistic point of view the liquid water consists of free water molecules and ice-like ranges where the tetrahedral water molecules are bonded with a hydrogen bond.

The hydrogen bond is partially orientated because of the hydrogen resonance between oxygens (Fig. 1/a). Its strength depends on the angle and length oscillation of covalent bonds inside the water molecules (Fig. 1/b). These covalent oscillations depend on the proton spin state. The magnetic resonance of two neighboring protons during the magnetic treatment could cause a spin transition (Fig. 2) from the singled ground state (anti-parallel orientation of spins) into the triplet excited state (parallel orientation of spins) which could indirectly lead to weakening of the hydrogen bond.

A direct return to the ground state is prohibited by the quantum theory. The return through the original transition, which demands an activation energy, explains a magnetic memory which has been observed to last several hours and even days after finishing the magnetic treatment. In other words, the available energy of practical static magnetic treatments is negligible in comparison with the thermal energy of atoms and molecules which relaxes inter-atomic changes in nanoseconds to microseconds if they are not caused by inner-atomic changes with longer relaxation times.

Such a weakened water molecule net would mean a weakened hydration of the main ions in natural waters, with the exception of K^+ and Cl^- ions, which dissolve by placing themselves into a vacancy of the original net with a strengthening of the net. On the other hand, some ions, which in natural waters participate in low concentrations and dissolve by forming their own hydration cover from free water molecules (i.e. Fe^{2+}) become more hydrated. According to this hypothesis, the proton magnetic-resonance measurements have confirmed the magnetically weakened hydration of $Ca(HCO_3)_2$ solutions and the intensified hydration of colloidal iron [26].

The changes in hydration partially explain modified $CaCO_3$ crystallization during and after MWT. In general, the crystal growth is performed with several successive steps, from which the slowest one is the crystal-growing rate-determining step. In the case of $CaCO_3$, the partial dehydration of crystal-forming ions is the slowest growth step [27]. So, the magnetically weakened hydration of Ca^{2+} and HCO_3^- can lead to enhanced crystal growth of $CaCO_3$ and the formation of bigger crystals.

3 CONCLUSION

In many reports about MWT research ([28] to [31]) the importance of iron components has been highlighted. Some MWT devices could be considered only as a sacrificed anode (the dissolving of which is accelerated by a magnetic field), but in most cases

vendar pa se v večini primerov vloga komponent z deležem železa ne more pojasniti na ta način. V primerih dinamične MOV pride do magnetohidrodinamičnih premikov kristalotvornih ionov k rastoči površini zaradi Lorentzove sile, kar bi lahko pospešilo in spremenilo kristaljenje vodnega kamna. Ti premiki so večji pri ionih z višjo valenco in manjšim radijem in so različno usmerjeni ob dispergiranih delcih vodnega kamna [32]. Magnetohidrodinamični premiki Fe^{2+} , kot pragovnega zavirala kalcitne rasti, bi lahko delno pojasnili zvišan delež aragonita, medtem ko bi moralo biti pospešeno obarjanje $CaCO_3$ ob navzočnosti mikrokristalov železovega hidroksida nekako povezano s spremembami pH , ki imajo močan vpliv na rast $CaCO_3$ in bi lahko bile povzročene z magnetno spremenjeno hidratacijo površin železovega hidroksida.

the role of iron components could not be explained only in this way. In the cases of dynamic MWT, the magnetohydrodynamic shifts of crystal – forming ions towards the growing crystal surface occur due to Lorentz force and could accelerate and modify the scale crystallization. They are higher for ions with higher ion valence and lower radius, and have different orientation at dispersed scale particles (Lipus [32], 1998). Magnetohydrodynamic shifts of Fe^{2+} ions as threshold inhibitors of calcite growth could partially explain raised part of aragonite. While at the acceleration of $CaCO_3$ precipitation in the presence of iron-hydroxide micro-crystals should be connected with pH changes, which have a strong influence on $CaCO_3$ growth and could be caused by magnetically modified hydration of iron-hydroxide surfaces.

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