Applications of ChemApp models to mine water chemistry

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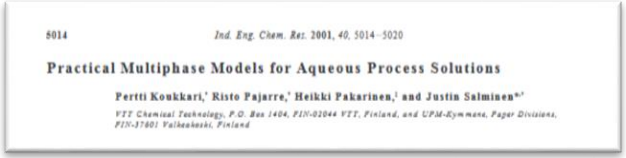
Background: Multi-phase models for fibre suspension chemistry


5014 *Ind. Eng. Chem. Res.* 2001, *40*, 5014–5020

Practical Multiphase Models for Aqueous Process Solutions

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- Aim: To use $CaCO_3$ as filler in paper. To understand the aqueous and fibrous (acidic) phases
- Thermodynamic database:
  - Cations: $Na^+/K^+/H^+/Ca^{+2}/Mg^{+2}/Mn^{+2}/Fe^{+2}/Fe^{+3}/Al^{+3}/Ni^{+2}/Zn^{+2}/Cu^{+2}$
  - Anions: $Cl^-/OH^-/CO_3^{-2}/SO_4^{-2}$
  - Temperatures 25-95 °C
  - Concentrations up to 6 mol/kg
  - Pitzer formalism used
- Applications: Neutral conversion of paper machines, controlling pH of pulp suspensions, pulp washing studies, in-situ precipitation of PCC

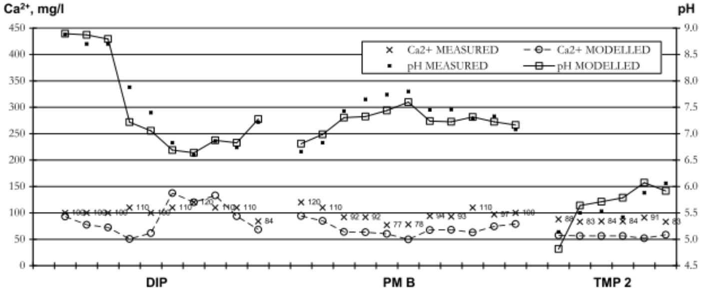


Fig 6. **Production of low brightness paper grades:** Modelled and measured values of dissolved calcium (Ca^{2+}) and pH at the PM B line (x-axis corresponds to the process points in the DIP, PM B and TMP 2 processes).

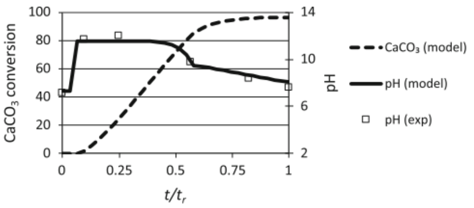


Fig. 6 Modelled and measured pH in the PCC reactor together with modelled $CaCO_3$ conversion rate as function of reduced residence time

Koukkari, P. *et al.* (2001) 'Practical Multiphase Models for Aqueous Process Solutions', *Industrial & Engineering Chemistry Research*, 40(22), pp. 5014–5020. doi: 10.1021/ie010236r.
Kalliola, A. *et al.* (2012) 'Multi-phase thermodynamic modelling of pulp suspensions: Application to a papermaking process', *Nordic Pulp and Paper Research Journal*, 27(03), pp. 613–620. doi: 10.3183/NPPRJ-2012-27-03-p613-620.
Koukkari, P., Pajarre, R. and Kangas, P. (2018) 'Thermodynamic affinity in constrained free-energy systems', *Monatshefte für Chemie - Chemical Monthly*, 149(2), pp. 381–394. doi: 10.1007/s00706-017-2095-5.

Case #1: Neutralisation of acid mine drainage

- Target: Treatment process of acidic mine drainage (AMD) for sulfate removal: 3000 -> 1000 mg/l
- Key cations: $Na^+/H^+/Ca^{+2}/Mg^{+2}/Mn^{+2}/$
- Key anions: $Cl^-/OH^-/CO_3^{-2}/SO_4^{-2}$
- Temperature: 25°C
- Validation of the applicability of previously developed database for mine water treatment against literature data
- Case: Olifants River AMD

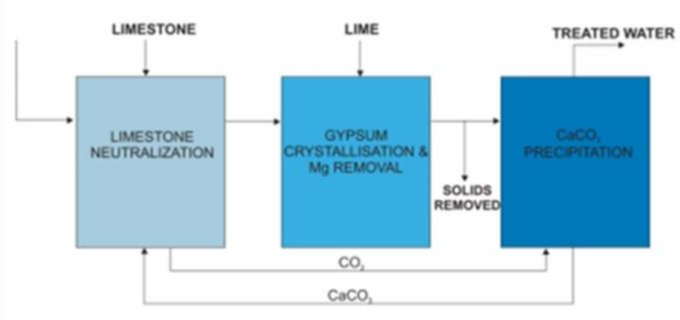


Figure 26. Oliphant River AMD treatment (Geldenhuys et al., 2003; INAP, 2003).

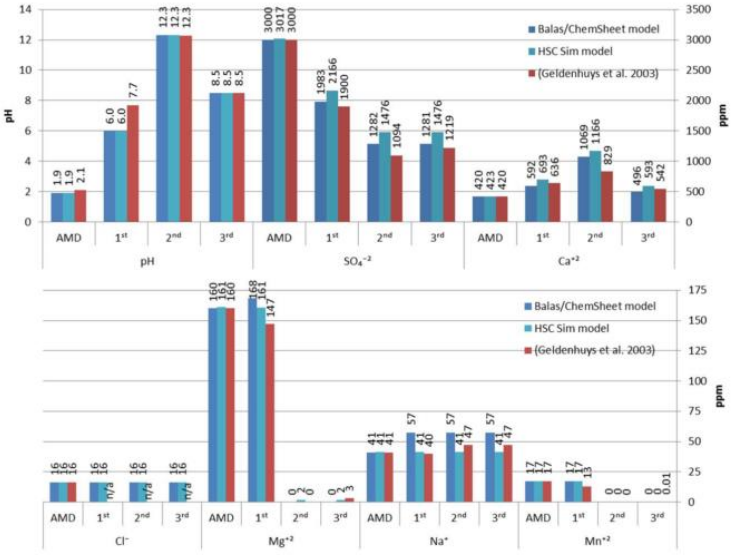


Figure 29. Composition of Olifants river AMD before treatment (AMD), after limestone treatment (1st), after lime treatment (2nd), and after CO^2 treatment (3rd). Validation data by Geldenhuys et al. (Geldenhuys et al., 2003).

Pajarre, R., Koukkari, P. and Kangas, P. (2018) *Industrial and mine water chemistry - Advanced aqueous database for modelling industrial processes*, *VTT Technology*. Espoo. Available at: http://www.vtt.fi/inf/pdf/technology/2018/T321.pdf.

Case #2: Talvivaara mine leachate and water treatment

- Target: Neutralisation of mine leachate after metals recovery for sulfate control: 100 000 -> 10 000 mg/l
- Key cations: Na$^+$/H$^+$/Ca^{+2}/Mg^{+2}/Mn^{+2}/Fe^{+3}/Al^{+3}
- Key anions: OH$^-$/CO$_3^{-2}$/SO$_4^{-2}$
- Temperature: 25-50°C
- Validation of the applicability of previously developed database for hydrometallurgical processes against literature data (Hietala 2012)
- Case: Talvivaara mine

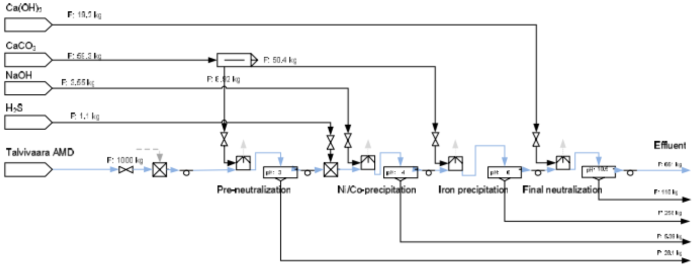


Figure 30. BALAS/ChemSheet model of the Talvivaara metal recovery and waste water treatment. Figures are given per 1000 kg of treated water.

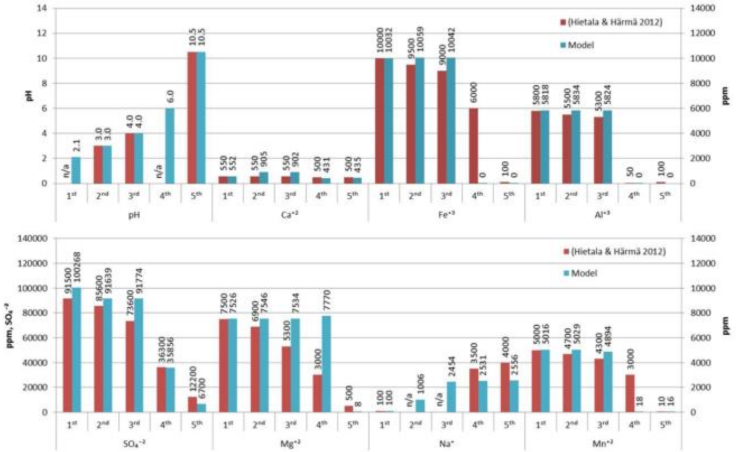


Figure 31. Composition of Talvivaara leachate before treatment pre-neutralisation (1st), after pre-neutralisation with limestone (2nd), after Ni/Co-precipitation (3rd), and after iron precipitation (4th), and after final neutralisation (5th). Validation data by Hietala and Härmä (2012).

Pajarre, R., Koukkari, P. and Kangas, P. (2018) *Industrial and mine water chemistry - Advanced aqueous database for modelling industrial processes*, *VTT Technology*. Espoo. Available at: http://www.vtt.fi/inf/pdf/technology/2018/T321.pdf.

Case #3: Valorisation of Separated Solids from Mine Water Treatment

- Target: Development of technique for fractionating Mg from the mixed gypsum precipitate
- Key cations: $H^+/Ca^{+2}/Mg^{+2}$
- Key anions: $OH^-/CO_3^{-2}/SO_4^{-2}$
- Temperature: 10-25°C
- Concept development for Mg recovery. Validation of proposed concept by experiments.
- Case: a Finnish mine

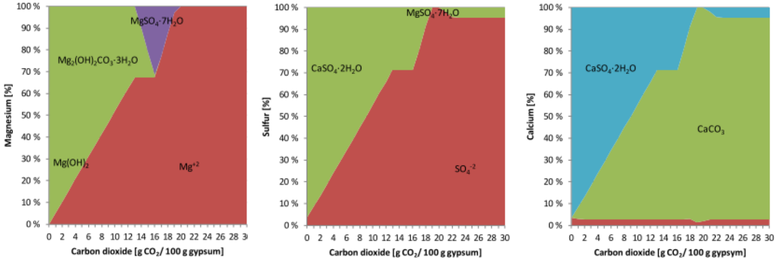


Figure 2 *Appearance of magnesium (left), sulphur (centre) and calcium (right) species within the chemical system during the carbon dioxide treatment of mixed gypsum sludge. Here the composition of raw material is 25% of $Mg(OH)_2$ and 75% of gypsum. Amount of water is 1000 g per 100 g of solids.*

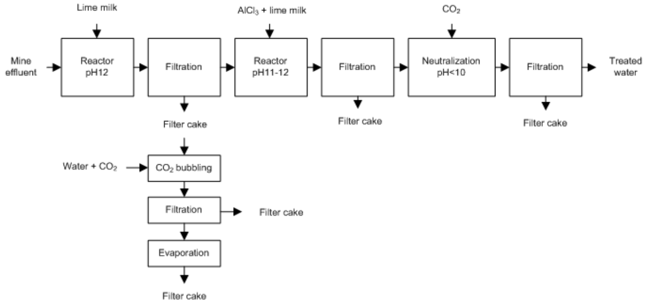
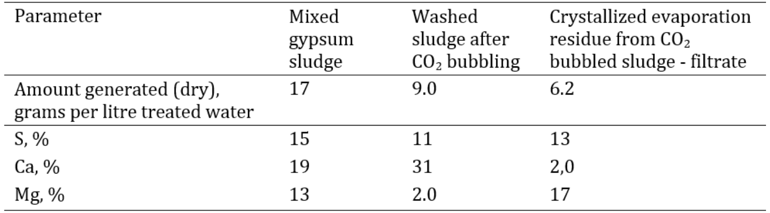


Figure 1. *Studied concepts for Mg recovery and sulphate removal.*

Table 4. *Characteristics of solids formed in different stages of concept A.*



Parameter	Mixed gypsum sludge	Washed sludge after CO_2 bubbling	Crystallized evaporation residue from CO_2 bubbled sludge - filtrate
Amount generated (dry), grams per litre treated water	17	9.0	6.2
S, %	15	11	13
Ca, %	19	31	2,0
Mg, %	13	2.0	17

Kaartinen, T., Kangas, P. and Arnold, M. (2017) 'Valorisation of Separated Solids from Mine Water Treatment', in Wolkersdorfer, C. et al. (eds) *13th International Mine Water Association Congress (IMWA 2017)*. Lappeenranta, Finland, pp. 55–63.

Case #4: Aluminium recovery from raffinate

- Target: Valorisation of aluminium (5000 mg/l) from raffinate from metals recovery plant. Utilisation of in-situ precipitated Al for ettringite precipitation.
- Key cations: H^+/ Na^+/Ca^{+2}/Mg^{+2}/Al^{+3}
- Key anions: OH^-/CO_3^{-2}/SO_4^{-2}
- Temperature 25-50°C
- Concept development for Al recovery. Validation of proposed concept by experiments.
- Case: Sotkamo mine

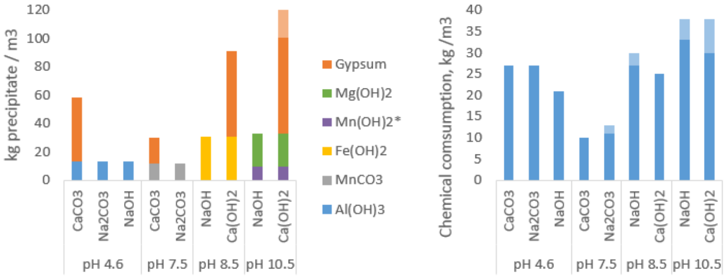


*Figure 2. Summary of screened concepts for metal recovery. Precipitates after each treatment, kg/m³ (left). * Mn(OH)₂ precipitates only if it is not precipitated as carbonate at pH 7.5. Chemical consumption in each treatment, kg/m³ (right). Light orange and light blue indicates range of gypsum precipitate and the range of chemical usage. Previous steps affect slightly on amounts of used chemicals.*

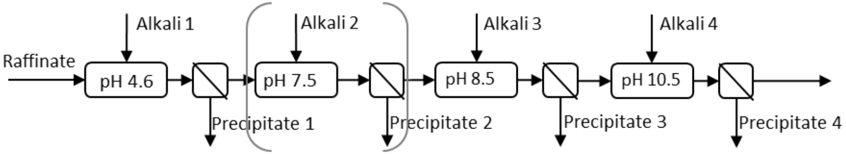


Figure 1. Studied concepts for fractionating metals (top) and for calcium removal (bottom),

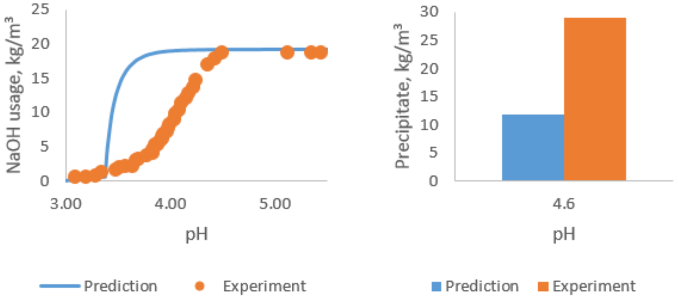


Figure 6. Treatment of raffinate 2 with NaOH. Alkali usage as a function of pH (left), and precipitate after treatment (right).

Nappa, M., Kiipula, K., Kyllönen, H., Kaartinen, T., Pajarre, R. and Kangas, P. (2018) ‘Valorisation of effluent from metal recovery plant’, in *14th International Mine Water Association Congress (IMWA 2018)*. Pretoria, South Africa.

Case #5: Calcium removal prior reverse osmosis

- Target: Increase water recovery (WR) during reverse osmosis by reducing scaling tendency. Removing Ca (500 mg/l) prior RO.
- Key cations: H$^+$/ Na$^+$/Ca^{+2}
- Key anions: OH$^-$/CO$_3^{-2}$/SO$_4^{-2}$
- Temperature 25-50°C
- Concept development for Ca separation. Validation of proposed concept by experiments.
- Case: Sotkamo mine

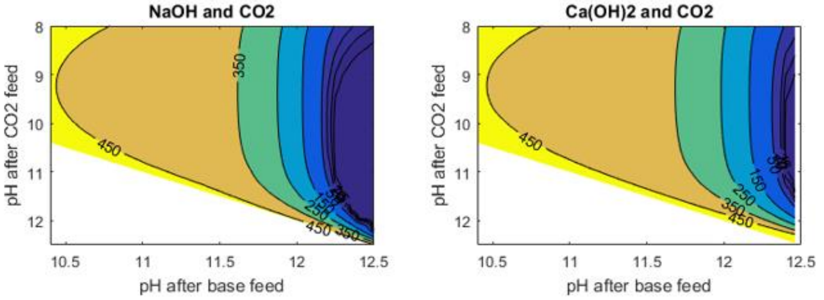


Figure 3.Treatment of NP overflow with base (NaOH left and Ca(OH)$_2$ right) and CO$_2$. Calcium ion concentrations in solute as function of pH after base feed and pH after CO$_2$ feed, mg/l. Bottom figures are

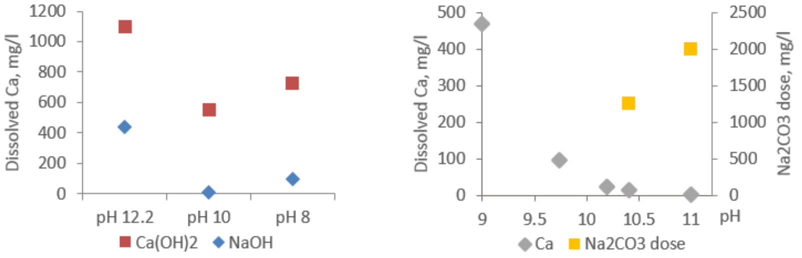


Figure 7. Dissolved calcium content after different experimental treatments. Sequential treatment with NaOH or lime up to pH 12.2 continued with acidification (left), Na$_2$CO$_3$ as treatment chemical (right).

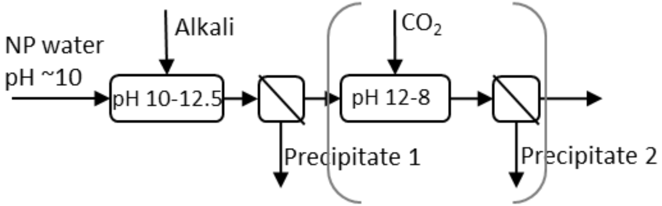


Figure 1. Studied concepts for fractionating metals (top) and for calcium removal (bottom).

Nappa, M., Kiipula, K., Kyllönen, H., Kaartinen, T., Pajarre, R. and Kangas, P. (2018) 'Valorisation of effluent from metal recovery plant', in *14th International Mine Water Association Congress (IMWA 2018)*. Pretoria, South Africa.

Case #6: Evaluation of alternative alkalis within metals recovery plant

- Target: Reduce sulfate content of effluent (from 4500 mg/l) from metals recovery plant by utilising alternative alkalis for pH control.
- Key cations: $Na^{+}/H^{+}/Ca^{+2}/Mg^{+2}/Mn^{+2}/Fe^{+3}/Al^{+3}$
- Key anions: $OH^{-}/CO_3^{-2}/SO_4^{-2}$
- Temperature: 25-70°C
- Computational assessment validated with experiments.
- Case: Sotkamo mine

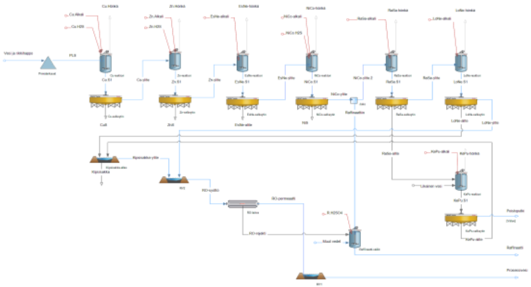


Figure 1. Metals recovery plant at Sotkamo mine.

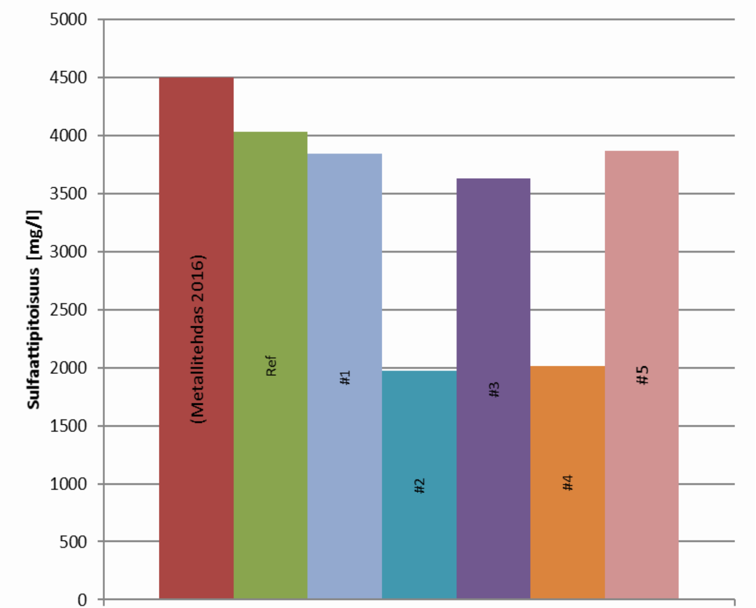


Figure 2. Sulfate content of treated process water; various alkalis applied for pH control within metals recovery plant.

Kangas,P., and Koukkari P., (2016) ‘Kehittyneiden liukoisuusmallien avulla pienempiin sulfaattipäästöihin’, Poster in Terramamen vesienhallinnan seminaari, 16.62016, Helsinki.

Key findings

- The developed database well applicable for describing industrial concentrates, brines and mine waters.
- Thermodynamic equilibrium assumption is often valid for aqueous processes.
- ChemSheet/ChemApp can be incorporated as part of process modelling.
- Key cations (H^+/ Na^+/Ca^{+2}/Mg^{+2}/Al^{+3}) and anions (OH^-/CO_3^{-2}/SO_4^{-2}) are often main species in solutions after removal target metals (Cu, Zn, Ni, Co, …).
- Database can be extended case by case with additional metals if needed
- Industrial processes are operating in evaluated temperatures (25 – 90°C) but commonly available data often applicable in lower temperatures (~ 25°C).

Key difficulties

- Kinetic phenomena (precipitation, dissolution) need to be incorporated to the models => Use e.g. Constrained Free Energy (CFE) technique (Koukkari & Pajarre 2006)
- Super-saturation (e.g. gypsum) => Utilise affinity based constraints (Koukkari 2017)
- Very concentrated solutions (> 6 mol/kg) need special models => (Pajarre 2018)
- Redox-phenomena as part of models (ferrous vs. ferric; Mn; As)
- Sulfide data of aqueous solutions is uncertain
- Expansion of the amount of recovered metals (technology metals); no activity data in solutions currently available

More details about aqueous database utilised

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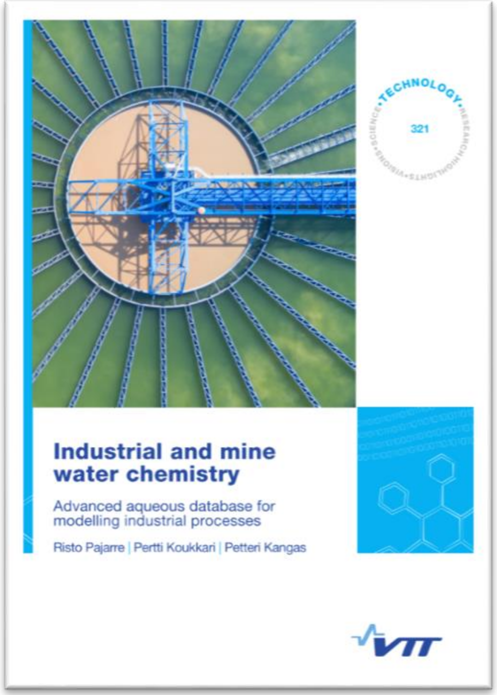
http://www.vtt.fi/inf/pdf/technology/2018/T321.pdf.



Industrial and mine water chemistry

Advanced aqueous database for modelling industrial processes

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