

Effects of Metal Oxides on the Crystallization of BaSO₄ in a Vibrated Batch Crystallizer System

N. Karaman, S. Muryanto, J. Jamari, A. P. Bayuseno

Abstract: Scale formation of BaSO₄ (barite) is a serious and persistent problem in a petroleum industry. The scale may severely hamper industrial processes through clogging the equipment, blocking the piping system, reducing the transfer of heat and material, which can lead to total breakdown and substantial financial losses. Hence, various methods have been applied to prevent the scaling of barite. This work reports a vibrated-batch lab crystallization to examine the influence of copper oxide (CuO) and zinc oxide (ZnO), an increasing temperature and mechanical vibration at 4.00 Hz and 8.00 Hz frequencies on crystallization kinetics and morphology of barite. The experiments using an experimental rig which was equipped with mechanical vibration to vibrate the rig under the heating program control. The inducing of vibration at 4.00 Hz and 8.00 Hz frequencies resulted in increasing rate scale deposition, whereas barite is the main crystal of the precipitated product which could be validated by the XRD Rietveld method. A morphological investigation by SEM confirmed that barite has mainly rosette-like crystal with the smaller size of order 5 μm. A new habit crystal of barite under the influence of vibration could be observed, and here an increasing vibration and additive concentrations made a reduction of scale deposition and providing more dense crystal morphology. The current findings suggest that the presence of mechanical vibration can be used to elucidate the mechanism of crystallization as well as the control of the morphology of barite. In practical terms, metal oxides could be potential as a scale inhibitor, while the mechanical vibration can be used to prevent the barite formation on pipes or mechanical equipment of the petroleum industry.

Keywords: Barite; Metal Oxides; Vibration; XRD Rietveld metho.

I. INTRODUCTION

In offshore oil production, barite favor to form when sulfate ions raise from wellbore and then meet to barium present abundantly in the injection of sea water [1], [2]. Barite accumulating on the metal surface makes it almost insoluble and is difficult to remove. This barite scale can also make troublesome in many piping systems flowing with the sea water. Moreover, such a scaling process is commonly evaluated in reverse osmosis application [3]. Also, the scale could be formed in the industrial petroleum components during oil drilling processes, which could be a negative effect of restriction of flow performances [4], [5].

Revised Manuscript Received on February 24, 2020.

^{*}Corresponding author.

N. Karaman, Department of Chemical Engineering, UPN "Veteran" Jatim, Gunung Anyar, Surabaya, Indonesia.
E-mail: novel_karaman05@yahoo.com.

S. Muryanto, Department of Chemical Engineering, UNTAG University in Semarang, Bendhan Dhuwur Campus, Semarang, Indonesia.
E-mail: stefanusmuryanto@yahoo.com.au

J. Jamari, Department of Mechanical Engineering, Diponegoro University, Tembalang Campus, Semarang, Indonesia.
E-mail: j.jamari@gmail.com

***A. P. Bayuseno**, Department of Mechanical Engineering, Diponegoro University, Tembalang Campus, Semarang, Indonesia.
E-mail: apbayuseno@gmail.com,

This condition has been intensively investigated by many researchers, in particular, focused on the use of chemical additives for controlling its solubility and the mechanism of crystal growth [5]. Conversely, barite can be synthesized to beneficially provide raw material which is commonly used for paint and pigment industry [6]. For instance, a high-quality white pigment of paint and painting could be provided by zinc-barite. However, the alteration of physicochemical properties may influence the deposition of scales, whereas the new fluid composition and conditions during the mixing process may lead to more problems in the production process. It is really necessary to monitor deposition conditions and the composition of fluids produced at each point in order to predict the occurrence of a particular problem.

Furthermore, in many industrial and oil drilling process, barium sulfate (barite) grows from the resulting solution relating to the heterogeneous crystallization [5]-[8]. Barite scaling is a complex crystallization process of involvement of mass transfer levels and energy conversion in supersaturated solutions. In particular, barite solubility depends on the temperature, but independently on the pH solution. Additionally, many factors may influence the crystallization process, on which stirring speed and the chemical additives have the most significant factor in the crystallization process [9], [10]. Here additives in industrial crystallization can be used for controlling the crystal growth and altering morphological crystal [11].

Specifically, barite scaling may be formed in flow-induced vibration, which can be generated by mechanical vibration originating from a blower, extruder, generator, turbine, and compressor. These conditions are affected by a number of complex physical and chemical factors [12] on which hydrodynamics of operating conditions potentially leads the flow induced vibration. The mechanical vibration may influence the mechanism of crystal growth in the solution. Mechanism of mechanical vibration in controlling scale formation may be contributed by the hydrodynamic forces. Moreover, the scale growing on the metal surface due to the hydrodynamic force is found in almost all industries and points out that the topic is urgent to investigate. It was reported that the increase in hydrodynamic force leads in increasing scale deposited on the surface material [13]. Likewise, the presence of chemical additives in the solution involves a chemical reaction to control the growth of scale. Here the chemical additives can be used for scale inhibitors against calcium carbonate and calcium sulfate, which may be also effective in controlling strontium and barium derived scales.

Effects of Metal Oxides on the Crystallization of BaSO₄ in a Vibrated Batch Crystallizer System

However, the effective combination of dosage in chemical inhibitor and frequency of mechanical vibration for scale deposited have not been observed previously.

The present research investigated barite scale formation in the solution by two metal oxide crystallizer and induced vibration. Two metal oxides (CuO and ZnO) were chosen in the present work to influence barite scale formation, because they have likewise been known as mineral association with barite in nature. Analytically based laboratory methods such as X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM) were used to complement the synthesis experiments.

II. METODOLOGY

Material for barite forming solution

Barium [Ba²⁺] was prepared in the solution at a concentration of 3500 ppm (3500 mg/l), whereas sulfate [SO₄] concentration was set up its stoichiometry accordingly. Barium and sulfate reagents were then dissolved separately in distilled water. Each solution was filtered using paper of 0.22 μm micropore and then stored in a covered container for subsequent experiments. The selected material of the vessel would be reacted with the solution. Subsequently, two metal oxides (CuO and ZnO) (0, 10 and 20 ppm) were prepared to mix with the solution.

Barite was formed in a vibrated batch crystallizer with Pyrex glass of 1 L solution at various temperatures (30, 35, 40 and 50 °C). Supersaturated solutions for crystal growth experiments were obtained by the slow flowing of equal volumes (254.8 x10⁻⁴ M) of barium chloride and sodium sulfate (purchased from Merck®) solutions, which were subsequently congregated in a glass beaker. The beaker was placed on a vibrating table to provide disturbing and homogenizing necessary for the solution (Figure 1).

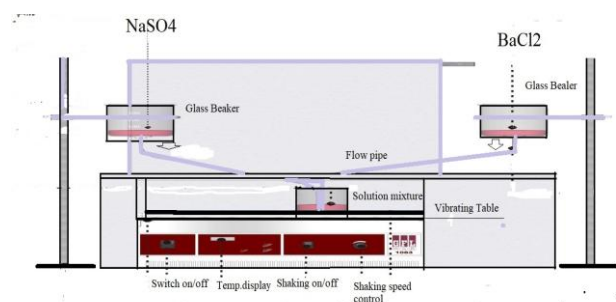
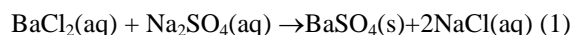


Fig. 1 Experimental set-up for barite crystal forming solution

In this way, each solution was allowed to flow until the beaker was almost full with the solution. Subsequently, the beaker was vibrated vigorously for about 10 (ten) seconds for initial stirring. Then, vibration frequency was set up; 0.00; 4.00 and 8.00 Hz. These vibration values were selected because the initial experiment suggested that the values could fully homogenize the solution without any discharging, or otherwise damage, of the crystals developed. Accordingly, barite would be formed according to the chemical reaction below:



The impact of additives on the precipitation rate of barite was investigated by measuring the mass over time as a deposition rate. Chemical inhibitors with amount 0, 10 and 20 ppm were diluted to the mixing solution every experiment. After finishing the one hour experiments, the scale was precipitated at the bottom of the beaker and was collected in the paper filter for drying in an electrical heater at 60 °C for six hours. The course of the experiments was followed by removing homogeneous particles at various times and quickly filtered through millipore filters of 0.22 μm pore size. The scale mass was then weighed on an analytical balance (Ohaus AR-2140) before and after drying.

Mineral characterization of barite

XRD data for mineral qualification and quantification was collected using Cu-Kα monochromated radiation in a conventional Bragg-Brentano parafocusing geometry by Rigaku SmartLab X-Ray Diffractometer. The data were then conveyed into a PC-based search match program for identifying crystalline phases. In this way, the peak positions and peak heights were matched with the database of International Centre for Diffraction Data-Powder Diffraction File (ICDD-PDF) CIF NO: 01-076-0213. The qualitative identified phase was then justified by the Rietveld method using FullProf-2k software version 3.30. The crystal structure model for Rietveld refinement was obtained in the literature of American Mineralogist crystal structure database (AMCSD).

Prior to a morphological analysis by SEM (scanning electron microscope), samples were mounted on a circular aluminum holder and finally sputtered with carbon. Morphology of crystalline product was investigated by SEM (FEI Inspect S50) with an acceleration voltage of 20 kV. Images were taken using a Megaview III digital camera (EMSIS GmbH).

III. RESULTS AND DISCUSSION

Influence of induced vibration on scale deposition rate

The results of the scale deposition rate of barite were presented in Table 1. Scale deposition rate without additive was obtained at 1.3126 gr.m⁻².h⁻¹ and increased to 1.3384 gr.m⁻².h⁻¹ and 1.5823 gr.m⁻².h⁻¹ as the vibration affected in 0, 4 and 8 Hz. This increasing value is supposed to be contributed by hydrodynamic forces coming from the induced vibration in the solution. These results are in agreement with the reported data [13]. In this work, the hydrodynamic force was generated by the rotation of cylinder electrode showing that the elevated rotation speed of cylinder electrode from 1000 rpm to 3000 rpm made the scale deposition rate of calcium sulfate increasing from 0.92 gr.m⁻².h⁻¹ to 1.62 gr.m⁻².h⁻¹ [13]. Likewise, the increasing temperature lead to a reduction of deposition rate, which may relate to increasing solubility of barite. Here, the scale deposition results were obtained in the case of without additive providing the highest value among others. Besides the presence of additives (CuO and ZnO) made a decreased scale formation process.

Further, the presence of mechanical vibration has a significant contribution to the deposition rate on the scale on the bottom. The combining effects of parameters (temperature, vibration frequency, and additives) could control the overall growth rate of the scale, and under such conditions, the linear rate of change was obtained, whereas a falling rate or asymptotic could be obtained from the linear line [14]. The asymptotic behavior of scaling could be observed in the study, because the rate of deposition may be balanced by the flowing fluid [15]. Here the significant effect of temperature (30 °C) and vibration frequency of 8 Hz and 200 ppm additives on deposition rate was considered as selected factors for the subsequent crystal habit and morphology investigations.

Crystal habit due to the presence of additives and mechanical vibration

The Rietveld refinement results of all samples confirmed that the pure barite crystal could be obtained and matched to the reference of the barite crystal structure model [16]. Figure 2 presents the Rietveld plots of the samples obtained from the solution in the absence of vibration and additives. Obviously, XRD diffractograms of all samples show that the crystal barite could be grown from all mother solution with and without additives and induced mechanical vibration (Fig. 3a,b). Moreover, the presence of additives and the mechanical vibration may influence of the XRD relative intensities. In particular, the only relative intensity of (200) peak to (401) peak was investigated. In this way, the crystal morphology and habit of barite could be examined through changing the values of XRD relative intensity of (200) peak and (401) peak. Alteration in the XRD relative intensity of each peak and its crystallite size when adding concentrated CuO and ZnO (20 ppm) and under induced vibrated condition (8 Hz) are presented in Table 2.

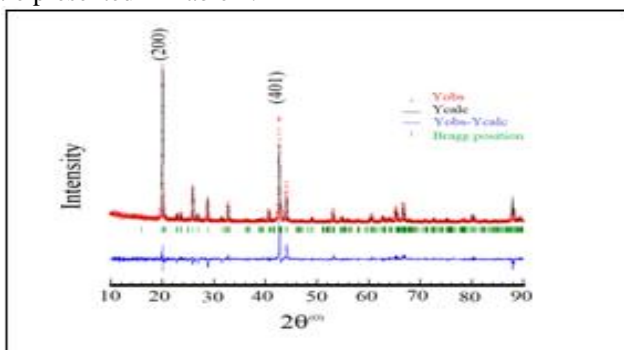


Fig. 2. XRD Rietveld plots of barite formed in the solution in the absence of additives and vibration

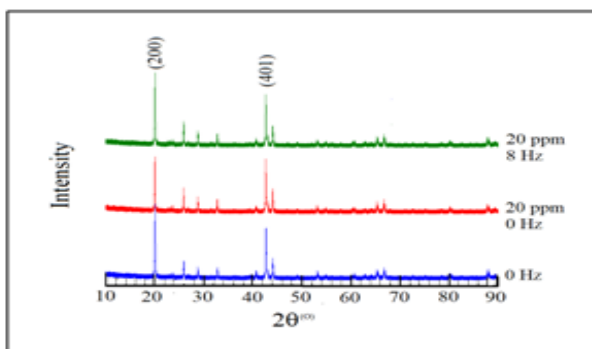


Fig. 3a. XRD diffractogram for barite formed in the solution with CuO and induced mechanical vibration

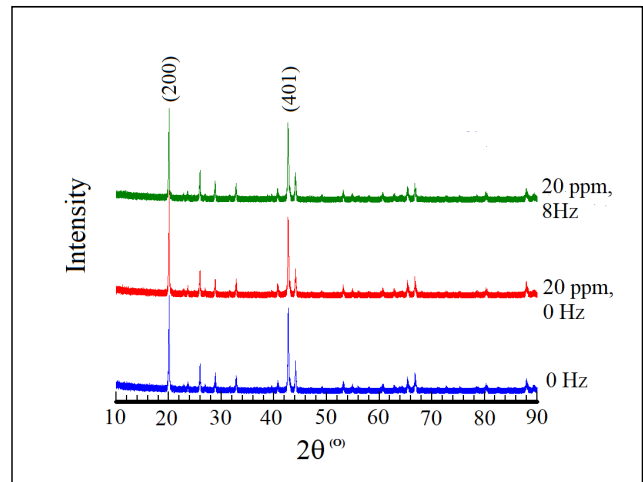


Fig. 3b. XRD diffractogram for barite formed in the solution with ZnO additives and induced mechanical vibration

Further, the crystallite size of barite could be estimated using formula of the Debye–Scherrer as follow:

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (2)$$

Where D, λ, β and θ are the average diameters, the X-ray wavelength, the half width of the peak (full width at half maximum-FWHM) and the Bragg’s diffraction angle respectively. In view of the XRD relative intensity of (200) and (401) peak, accordingly, the average particle size of barite was calculated and the results are presented in Table 2.

Apparently, the barite crystal contains aggregate of nano crystallite size. Conversely, morphology of barite examined by SEM is shown in Fig.4. In most cases, the precipitating solid has dominant rosette-like crystals with small aggregates. Under no vibration conditions, coarse crystals with crystal size reached to 5 μm order could be observed (Fig. 4a). These results are suggested to be controlled by slow and precise growth resulting from increasing solubility by increasing temperature. In the presence of CuO and ZnO (20 ppm) under the influence of vibration, rounded rosette crystals could be formed (Fig 4b-e).

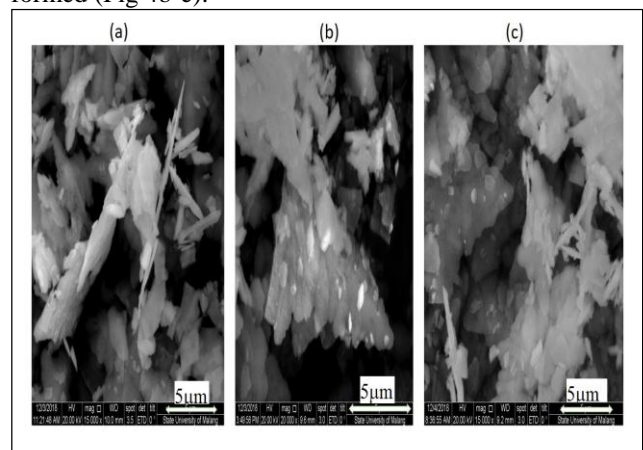


Fig. 4. SEM micrographs of barite crystal in: a) the absence of additive and vibration; b) 20 ppm CuO additive; c) the presence of 8 Hz vibration and 20 ppm CuO additive

Table-I: Scale deposition rate (g) of barite at varying temperature without additive and with additive of 20 ppm

Temp(°C)	Additive ZnO			Additive CuO			No Additive		
	0 Hz	4 Hz	8 Hz	0 Hz	4 Hz	8 Hz	0 Hz	4 Hz	8 Hz
30	1.2626	1.2720	1.2847	1.2837	1.2926	1.3038	1.3126	1.3384	1.5823
35	1.2517	1.2618	1.2820	1.2742	1.2860	1.2901	1.3051	1.3291	1.5272
40	1.2484	1.2524	1.2801	1.2678	1.2775	1.2870	1.3029	1.3122	1.4889
50	1.2329	1.2436	1.2795	1.2434	1.2690	1.2785	1.3007	1.3040	1.4669

Table-II: XRD Relative intensity and crystallite size of barite obtained from the experiments

Sample	2 θ	(hkl)	Relative Intensity	FHWM	Crystallite size (nm)
0 Hz 0 ppm	20.0431	(200)	100	0.1378	28.53
	42.6667	(401)	66.35	0.1574	36.45
0 Hz	20.0032	(200)	100	0.1378	25.94
20 ppm CuO	42.6241	(401)	98.94	0.0984	69.75
8 Hz	20.03	(200)	100	0.1181	32.23
20 ppm CuO	42.6379	(401)	71.49	0.0984	65.56
0 Hz 0 ppm	20.0535	(200)	100	0.1378	29.30
	42.6797	(401)	85.13	0.0984	55.54
0 Hz	20.0584	(200)	100	0.1378	29.68
20 ppm ZnO	42.6769	(401)	81.26	0.0984	56.11
8 Hz	20.0448	(200)	100	0.1181	33.43
20 ppm ZnO	42.6655	(401)	85.71	0.1378	41.82

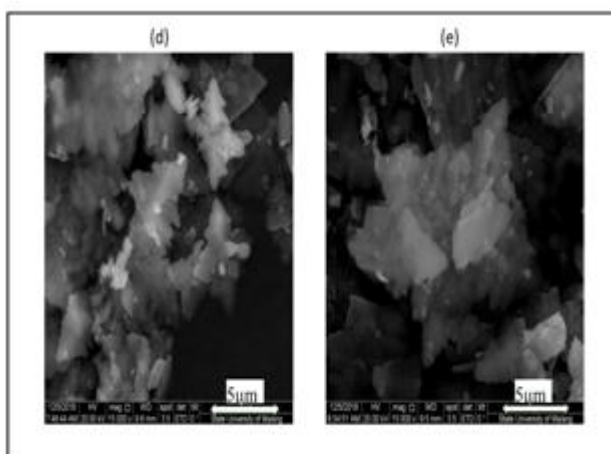


Fig. 4. SEM micrographs of barite crystal in: d) 20 ppm ZnO additive; e) the presence of 8 Hz vibration and 20 ppm ZnO

Moreover, more dense crystals could be resulted from the solution of raw materials in the presence of ZnO which may behave as a stabilizer (Fig. 4d,e). In contrast, when using concentrated 20 ppm CuO and 8 Hz frequency, irregular rosette-like or wide rosette-like crystals with relatively small sizes were dominant (Fig.4b,c). This result indicates high concentration of CuO may have an effect to change crystal habit by preventing crystal growth along (200) face indicating that the larger crystallite size was obtained in this face direction (Table 2). Similarly-shaped microcrystals or granular microcrystals assumed to be broken crystals or secondary crystals were also observed in most cases. Coexistence of coarse crystals and microcrystals degraded, especially in the case using CuO additive. However, a further

work of barite formation should be carried out in the case of a continuously induced flowing water with additives.

Further, this experimental approach is valuable in the evaluation of barite precipitation in the area of the petroleum industry and barite production in the paint industry. In particular, the morphology of barite and its prevention could be related to the particular additives and shear rate (as a measure of the flow conditions) [17]-[19]. In the geothermal power plant, for example, barite scale becomes a high risk for operational reliability and it must be treated properly [20].

Thus, the design approach of barite scale prevention requires comprehensive knowledge on supersaturation relating to the presence of additives and shear rate for solution movement generated by inducing flowing vibration [8]. Additionally, the supersaturation of barite could be achieved by mixing barium chloride and sodium sulfate solutions in the necessity, excessive concentration and it may be susceptible to the presence of additives, on which temperature, mixing speed and overall salt concentration strongly influence on the rate of barite precipitation [21], [22], [23],[24], [25].

IV. CONCLUSION

In this work, a unit based on dynamic vibration monitoring has been demonstrated to study the barite precipitation and prevention in the presence of CuO and ZnO. The XRD results confirmed the only barite could be precipitated from the solution with and without additives under influence of mechanical vibration. Barite has dominant rosette-like crystals with small aggregates as observed by SEM.

Obviously, the vibration application made in an increase the deposit rate of barite particles, yielding in smaller crystallite size. However, the barite particles grown in the presence of vibration and additives presented greater crystallite size with strong aggregation and denser than those formed without the vibration. The results suggested that the application of vibration in samples with barium cations and sulfate anions delays the induction time of barite precipitation. Consequently, the application of vibration and chemical additives can potentially prevent the formation of this barite deposited in pipelines in the petroleum industry.

ACKNOWLEDGMENT

The authors would like to thank the Universitas Pembangunan Veteran, Jawa Timur and to the Directorate General of Resources for Science, Technology & Higher Education, Ministry of Research, Technology and Higher Education (DIKTI) Indonesia for the financial supports and scholarships.

REFERENCES

1. W.J. Benston, I.R. Collins, I.M. Grimsey, G.M. Parkinson, and S.A. Rodger, "Nucleation, growth and inhibition of barium sulfate-controlled modification with organic and inorganic additives," *Faraday Discuss.* vol. 95, 1997, pp. 281-297.
2. K.S. Sorbie, and E.J. Mackay, "Mixing of injected, connate and aquifer brines in waterflooding and its relevance to oilfield scaling," *J. Pet. Sci. Eng.* vol. 27, 2000, pp. 85-92.
3. T.A. Hoang, H.M. Ang, and A.L. Rohl, "Effects of temperature on the scaling of calcium sulphate in pipes," *Powder Technol.* vol. 179, 2007, pp. 31-37.
4. M. Jamialahmadi, and H. Müller-Steinhagen, "Heat exchanger fouling and cleaning in the dihydrate process for the production of phosphoric acid," *Chem. Eng. Res. Des.* 85, 2007, pp. 245-255.
5. F. Jones, P. Jones, M.I. Ogdena, W.R. Richmond, A.L. Rohl, and M. Saunders, "The interaction of EDTA with barium sulfate," *J. Colloid. Interface Sci.* vol. 316, 2007, pp. 553-561.
6. H. B. Singh and K. A. Bharati, *Handbook of Natural Dyes and Pigments*, Woodhead Publishing India PVT. LTD, 2014.
7. E. Akyol, and M. Öner, "Inhibition of calcium oxalate monohydrate crystal growth using polyelectrolytes," *J. Cryst. Growth*, vol. 307, 2007, pp. 137-144.
8. A.J.B. Hennessy, and G.M. Graham, The effect of additives on the co-crystallisation of calcium with barium sulphate. *J. Cryst. Growth*, vol. 237-239, 2002, pp. 2153-2159.
9. E. Akyol, A. Bozkurt, and M. Öner, "The Effects of polyelectrolytes on the inhibition and aggregation of calcium oxalate crystallization," *Polymer Adv. Tech.* vol. 17, 2006, pp. 58-65.
10. Ö. Doğan, E. Akyol, and M. Öner, "Polyelectrolytes inhibition effect on crystallization of gypsum," *Cryst. Res. Tech.* vol. 39, 2004, pp. 1108-1114.
11. E. Akyol, M. Öner, E. Barouda, and K. D. Demadis, "Systematic structural determinants of the effect of tetraphosphonates on gypsum crystallization," *Cryst. Growth Des.* vol. 9, 2009, pp. 5145-5154.
12. C. Ruiz, V.H. Jaramillo, D. Mba, J.R. Ottewil, and Y. Cao, "Combination process and vibration data for improve condition monitoring of industrial system working under variable conditions," *Mech. Syst. Signal Pr.* vol. 66, 2014, pp. 699-771.
13. A. Quddus, and L.M. Al-Hadhrani, Hydrodynamically deposited CaCO₃ and CaSO₄ scales. *Desalination*, vol. 246, 2009, pp. 526-533.
14. S.-T. Liu, and G.H. Nancollas, "The kinetics of crystal growth of calcium sulfate dehydrate," *J. Cryst. Growth*, vol. 6, 1970, pp. 281-289.
15. M. D. G. de Luna, D. P. M. Rance, L. M. Bellotindos, and M-C. Lu, "A statistical experimental design to remove sulfate by crystallization in a fluidized-bed reactor," *Sustain. Environ. Res.* vol. 27, 2017, pp. 117-124.
16. R.T. Downs, and M. Hall-Wallace, "The American mineralogist crystal structure database (AMCSD). *American Mineralogist*, vol. 88, 2003, pp. 247-250.

17. Z. Amjad, *Inhibition of barium sulfate precipitation: effects of additives, solution pH, and supersaturation*, China Ocean Press, 1994: pp. 47-56.
18. A. Martinod, M. Euvrard, A. Foissy, and A. Neville, "Progressing the understanding of chemical inhibition of mineral scale by green inhibitors," *Desalination*, vol. 220, 2008, pp. 345-352.
19. Z. Belarbi, J. Gambya, L. Makhloufi, B. Sotta, and B. Tribollet, "Inhibition of calcium carbonate precipitation by aqueous extract of paronychiaargentea," *J. Cryst. Growth*, vol. 386, 2014, pp. 208-214.
20. D. Degering, M. Köhler, and M. Hielscher, "Vorkommen und Verhalten natürlicher radionuklide im aquifer, im fluid und in den ablagerungen der geothermieanlage neustadt-glewe," *Zeitschrift für Geologische Wissenschaften*, vol. 39, 2011, pp. 275-290.
21. K. Labiod, and S. Ghizellaoui, "Contribution to the inhibitors methods study of the scaling: chemical, electrochemical Processes in the presence of Ca(OH)₂, Na₂CO₃ and KH₂PO₄," *Energy Procedia*, vol. 18, 2014, pp. 1541-1555.
22. Y. Tang, W. Yang, X. Yin, Y. Liu, P. Yin, and Y. Wang, "Investigation of CaCO₃ scale inhibition by PAA, ATMP and PAPEMP," *Desalination*, vol. 228, 2008, pp. 55-60.
23. A.P. Bayuseno, and W.W. Schmahl, "Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods," *J. Cryst. Growth*, vol. 498, 15 September 2018, pp. 336-345.
24. D.S. Perwitasari, S. Muryanto, J. Jamari, and A.P. Bayuseno, "Kinetics and morphology analysis of struvite precipitated from aqueous solution under the influence of heavy metals: Cu²⁺, Pb²⁺, Zn²⁺," *J. Environ. Chem. Eng.* vol 6, Issue 1, February, 2018, pp. 37-43.
25. S. Muryanto, A.P. Bayuseno, W. Sediono, W. Mangestiyono, and Sutrisno, "Development of a versatile laboratory project for scale formation and control," *Education for Chemical Engineers*, vol. 7, Issue 3, August 2012, pp. e78-e84.

AUTHORS PROFILE



N. Karaman, is a PhD student in Mechanical Engineering Diponegoro University. He received his B.Eng and M.Eng in Chemical Engineering from Institute of Sepuluh November Technology, Surabaya, Indonesia. He conducts a current research on crystallization aspects of barium sulfate.



S. Muryanto, is a Professor in Chemical Engineering, UNTAG University in Semarang, Indonesia. He got his M.Eng.Sc in Chemical Engineering from Monash University, Australia and Ph.D from Curtin University of Technology, Australia. His research interest covers many aspects of applied crystallization in wastewater treatment.



J. Jamari, is a Professor in Mechanical Engineering at Diponegoro University, Indonesia. He received his B.Eng and M.Eng in Mechanical Engineering from Institute of Technology Bandung. He obtained his Doctoral in Laboratory for Surface Technology and Tribology, University of Twente, the Netherlands.



A. P. Bayuseno, is a Professor in Material Science and Engineering at Diponegoro University, Indonesia. His teaching interests are in Ceramics, and Materials Science and Engineering. Research interests cover many aspects of ceramics design, applied crystallography, including materials characterization and waste processing. He completed his master's and doctorate studies at Curtin University of Technology, Australia, and the Ruhr University of Bochum, Germany, respectively.