



Article Effect of Different Concentrations of NiMnGa Micro/Nanoparticles on the Kinetics of Natural Gas Hydration

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Abstract: To improve gas hydrate storage and transportation technology, ferromagnetic intermetallic compound NiMnGa particles with martensitic transformation endothermics were used to form micro/nanofluids with sodium dodecyl sulfate (SDS) to further strengthen the gas hydration process. In this work, the kinetic process of gas hydration in NiMnGa fluids with different concentrations (0, 0.1, 1, 2, and 3 wt.%) was investigated using a rotating magnetic field gas hydration separation experimental setup. The results show that the induction time of the 3 wt.% NiMnGa system was shortened by 98.3%, the gas consumption was increased by 50.5%, and the gas consumption rate was increased by 351.9% compared with the SDS system. Therefore, it is inferred from the mass transfer that NiMnGa micro/nanofluids can accelerate the formation of hydrates.

Keywords: natural gas hydrate; NiMnGa; micro/nanoparticles; particle concentration; kinetic characteristics

1. Introduction

Natural gas hydrates are a widely distributed clean energy source [1,2]. With the successful test mining of marine sediment hydrates in China, gas hydrates are expected to become a new generation of energy to displace oil, coal, and conventional gas. The development and utilization of gas hydrates has become essential to ensuring national energy security, promoting deep sea strategy, and achieving the double carbon goals. Gas hydrates are a non-chemometric cage-like crystalline substance formed by water and methane gas, known as combustible ice [3,4], making it a very clean energy source. Based on the advantages of mild formation conditions, high gas content, and safe storage and transportation [5,6], related scholars have proposed the safe storage and transportation of methane gas released via hydrate mining through hydration technology so as to alleviate energy tension [7–12]. However, there is a problem in the hydration process, namely, the mass transfer, which has long induction periods, slow formation rates, and high driving forces of hydrate formation [13].

Improving the kinetics of hydrate generation is one of the feasible factors for the industrialization of hydrate technology. Scholars have proposed many methods by which to improve the kinetics of hydrate generation through experimental studies, and the traditional chemical methods are mainly intended to reduce the surface tension of the liquid phase by adding kinetic enhancers to promote the formation of hydrates [14,15]. The typical kinetic additives mainly include SDS [16,17], amino acids [18,19], and sulfonated lignin (SL) [20]. The traditional physical hydration enhancement methods mainly include



Citation: Zhao, Z.; Wu, Q.; Li, Z.; Meng, H.; Elhefnawey, M.; Wang, X.; Wu, Q.; Li, L.; Zhang, B. Effect of Different Concentrations of NiMnGa Micro/Nanoparticles on the Kinetics of Natural Gas Hydration. *Processes* 2023, *11*, 3149. https://doi.org/ 10.3390/pr11113149

Academic Editors: Qingbang Meng, Zhenyuan Yin, Tao Yu, Bingbing Chen, Pengfei Wang and Ying Teng

Received: 9 October 2023 Revised: 29 October 2023 Accepted: 31 October 2023 Published: 4 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the stirring method, spraying method, bubbling method, and applied magnetic field method. In addition, some scholars have found that the properties of nanoparticles, such as high specific surface area and high thermal conductivity, can effectively enhance the heat and mass transfer in the hydration process [21–24], which can improve kinetic parameters, such as the hydrate conversion rate and gas storage, and promote hydrate generation.

Ghozatloo et al. [25] first found that 1 wt.% graphene reduced the induction time of 92.6% CH₄ gas hydrate by 61.07% and increased the storage capacity of the hydrate by 12.9%. Park et al. [26] used different concentrations (0.001–0.006 wt.%) of carbon nanotubes (MWCNTs) to improve CH₄ hydrate generation dynamics, where 0.004 wt.% of multiwalled carbon nanotubes resulted in milder phase equilibrium conditions for CH₄ hydrate, about 300% higher gas consumption than pure water, and a significant reduction in the CH₄ hydrate formation time. Arjang et al. [27] used a mixed solution containing sodium citrate and nanosilver to improve hydrate generation kinetics. Compared to sodium citrate solution, the induction time of the mixed solution with nanosilver was reduced by 63.6%, and the CH₄ gas consumption was increased by 7.4%. Rahmati-Abkenar et al. [28,29] discovered that an aqueous solution of Ag nanoparticles shortens the induction time of CH₄ hydrate by 97% compared with pure water, and that increasing the particle concentration can reduce the effect of surface tension on CH₄ hydrate formation. Aliabadi et al. [30] investigated the effect of 0.035 wt.% SDS and 1 wt.% CuO nanoparticles on methane hydrate formation, the results showed that the addition of nanoparticles reduced the induction time and increased the final hydrate conversion by 157.93% compared to pure water. Abdi-Khanghah et al. [31] conducted 0.05 and 0.1 wt.% ZnO + 0.03 wt.% SDS particle experiments on methane hydrate, wherein ZnO particles improved heat and mass transfer in the solution due to their large surface area and nucleation sites. The results showed that the addition of nanoparticles decreased the induction time of the hydration reaction and increased the hydrate conversion by 60.22%. Kakati et al. [32] conducted experiments on the kinetics of $CH_4 + C_2H_6 + C_3H_8$ hydrate formation in 0.1, 0.4, and 0.8 wt.% Al₂O₃/ZnO + 0.03 wt.% SDS solution nanofluids and found that the incorporation of nanoparticles increased the gas consumption, which was 121% higher than that of the pure water system, and the gas storage. Meanwhile, some scholars have treated the nanoparticles by means of grafting functional groups and solid-loaded coated surfactants to promote the kinetics of hydrate generation. Wang et al. [33] realized SDS-coated nanospheres (SDS@PSNS) and nano-Ag particles grafted on the surface of SDS@PSNS to prepare Ag&SDS-coated nanospheres (Ag&SDS@PSNS) in order to enhance its promoting effect on the formation of methane hydrates. The hydrate formation time with 0.1 mol/L Ag&SDS@PSNS was shortened from 422.7 min to 156.7–273 min, and the entire methane hydrate generation period can be completed within 50 min with the 0.2 mmol/L Ag&SDS@PSNS. Chen et al. [34] investigated the synthesis of SDS-coated Fe_3O_4 nanoparticles that were successfully used to promote hydrate formation and cycling experiments, and SDS-coated Fe₃O₄ promoted hydrate formation more effectively than bare Fe_3O_4 . With the 20 g/L SDS-coated Fe_3O_4 , the CH₄ storage was $130 \pm 5.9 v/v$, and the induction and reaction times were reduced to 77.6 \pm 24.1 and 36 \pm 3 min, respectively.

All of the above nanofluids belong to the category of non-phase-change nanofluids, and studies have shown that nanoparticles have a promotional effect on hydrate generation, and the promotional effect varies depending on the concentration, type, and size of nanoparticles. In addition, it is expected to further strengthen the promotional effect of nanofluids on hydrate generation by utilizing the heat-absorbing property of materials in the process of phase change to absorb the heat of hydrate generation. Yan et al. [35] investigated the solid-state storage, generation rate, and induction period of CH₄ hydrates in nTD slurry and found that the hydration rate was highest under the conditions of 5.26 MPa, 158.7 v/v conditions with the highest hydration rate, and a hydration time of only 78 min. Song et al. [36] investigated the growth rate of CH₄ hydrates in cement slurries containing 25–45 wt.% solid n-tetradecane in the range of pressures of 4.7–6.46 MPa and temperatures of 263.2–283.2 K. The growth rates of the hydrates ob-

tained using phase change material particles were increased by a factor of three to nine. Liu et al. [37] demonstrated that under the action of a specific magnetic field, the amount of hydrate formation significantly increases, the hydration rate can reach 100%, and the induction time can be greatly shortened from 9 h to 40 min; moreover, the polarity of the magnetic field, the strength of the magnetic field, and the number of iron wires all have an impact on the formation of hydrates. Sun et al. [38] found that the magnetic effect increases the nucleation rate of CO_2 hydrates, shortens the nucleation induction time, and increases the consumption and rate of CO_2 . This is mainly due to the magnetic field reducing the contact angle between the water and the solid surface, reducing the size and free energy of hydrate nucleation, thereby promoting hydrate nucleation.

At present, related studies at home and abroad have focused on the process of gas hydrate formation in non-phase transformation nanofluids. Ferromagnetic intermetallic compound NiMnGa micro/nanomaterials, first, have the characteristics of large specific surface area, small size, and magnetic characteristic [39]. Second, NiMnGa has phase transformation characteristics, can absorb heat when reverse martensitic transformation occurs, and can provide a good environment for hydrate growth, thus promoting hydrate formation [40,41]. In addition, the temperature and latent heat of NiMnGa phase transformation can be controlled in the experimental temperature range easily [42]. In addition, a peripheral rotating magnetic field is used in this work, which can disperse magnetic micro/nanoparticles in the solution and promote mass transfer. Therefore, in this paper, the NiMnGa alloy particles, which has magnetic, high thermal conductivity, and phase transformation heat absorption characteristics, is used to improve the mass and heat transfer constraints of the hydration process for the purpose of shortening the induction time and improving the gas storage capacity of hydrate formation [43].

2. Materials and Methods

2.1. Experimental Materials

High-purity nickel blocks (99.99%), electrolytic manganese (99.7%), and high-purity gallium (99.99%) were supplied by Zhongnuo New Materials (Beijing, China) Technology Co. Gas samples (G1: 60% CH₄, 32% N₂, 8% O₂; G2: 70% CH₄, 24% N₂, 6% O₂; G3: 80% CH₄, 16% N₂, 4% O₂) were supplied by Harbin Chunlin Gas Distribution Co., Ltd. (Harbin, China); SDS was supplied by Tianjin Bailunsi Biotechnology Co., Ltd. (Tianjin, China); pure water was home-made by laboratory Thermo Fisher Water Purifier (Waltham, MA, USA).

2.2. Experimental Apparatus

Based on the requirements of the NiMnGa for the experimental study of gas hydration separation kinetics, a set of rotating magnetic field gas hydration separation experimental apparatus, developed by the group, was used. The experimental and test system is shown in Figure 1. The high-pressure titanium alloy reaction kettle is equipped with two high magnetic steels on the outside, and controlling the spacing between the magnetic steels can generate a magnetic field in the range of $0 \sim 0.5$ T. The magnetic steel is fixed on a rotating electric platform, and the rotation of the magnetic field causes the magnetic particles to move uniformly and stably in the solution inside the reactor with a speed range of 0-200 r/min. A detailed introduction of the device can be found in reference [41].

2.3. Experimental Procedure

Based on the extensive research on material preparation process optimization conducted by the research group in the early stage, this article uses the ball milling method to prepare NiMnGa alloy particles, and the preparation steps are as follows [44–49]: (1) in a vacuum arc melting furnace, nickel blocks, manganese, and gallium are melted into alloy ingots in the ratio of Ni_{52.5}Mn_{22.5}Ga₂₅; in order to supplement the volatilization loss of Mn during the melting process, 5% Mn is added to the ingredient; (2) we perform homogenization and solid solution treatment on alloy ingots; (3) NiMnGa ingots are milled in a high-speed vibrating ball mill to obtain NiMnGa particles; and (4) we anneal the particles after ball milling. The NiMnGa-SDS micro/nanofluid was prepared by using NiMnGa micro/nanoparticles and SDS solution.



Figure 1. Rotating magnetic field gas hydration separation experimental setup.

The fluid Is prepared by using NiMnGa particles, SDS, and pure water. We place SDS and particles in 40 mL pure water (prepared by a secondary pure water analyzer, Pacific TII, Thermo Fisher, Waltham, MA, USA). Then, a dispersing machine (T18 digital TURRAX, IKA, Staufenim, Germany) was used to stir and disperse the solution in 12,000 rad/min for 90 s, and the treated solution was loaded into the reactor for later use. The detailed process of fluid preparation and the hydration experiment can be found in reference [41].

2.4. Determination of Kinetic Parameters

Using graphical method, the induction time is defined as the time required from the initial pressure reached to the first significant temperature increase and pressure decrease during the hydration reaction process.

Gas consumption Δn :

$$\Delta n = \frac{n_0 - n_t}{n_w} = \frac{\frac{P_0 v_0}{z_0 R T_0} - \frac{p_t v_t}{z_t R T_t}}{n_w}.$$
(1)

In the formula, n_0 and n_t represent the amount of gas substances in the reactor at the initial time and time t, respectively; n_w is the molar amount of water; P_0 and T_0 are the initial pressure and temperature values in the reactor, respectively; P_t and T_t are the pressure and temperature values in the reactor at time t during the reaction process, respectively; R is the gas constant; and Z_0 and Z_t are the compression factors at the initial time and time t, respectively.

Gas consumption rate *v*:

$$v = \left(\frac{d\Delta n}{dt}\right)_t \approx \frac{\Delta n}{dt}.$$
(2)

In the formula, *t* is the time difference between two certain moments.

3. Results

For phase transformation testing and characterisation of NiMnGa micro/nanoparticles using high-pressure differential scanning calorimetry, scanning clicks, and particle size analysis via a laser particle sizer, the results of determination, characterisation, and analysis are given in reference [48].

In order to optimize the mass transfer effect of NiMnGa micro/nanofluids on the hydration process of natural gas, a vertical rotating magnetic field was set outside the titanium alloy high-pressure reactor used in this paper. The magnetic field rotation drives the NiMnGa alloy particles in the reactor to flow in the liquid phase, and the purpose of the uniform dispersion of particles is achieved by adjusting the magnetic field size and rotation speed. Under the premise of energy saving, it is found that the minimum rotational speed and the minimum magnetic field that can make the particles flow uniformly and disperse uniformly in the liquid phase are 100 rpm and 0.09 T, respectively. In this paper, the magnetic properties of NiMnGa alloy particles were tested via a physical property measurement system (PPMS-9, Quantum Design) under magnetic fields of 0 T and 0.09 T, respectively. The test temperature control speed was 5 °C/min, the magnetic field resolution was 0.2 mT, and the temperature range was $-50\sim120$ °C.

The gas hydrate formation process was conducted at 6.2 MPa and 2 °C. The experiments were carried out in the SDS system (NiMnGa particle Conc. 0%) and the NiMnGa-SDS system with different concentrations (NiMnGa particle Conc. 0.1, 1, 2, and 3 wt.%) using three different gas samples (G1, G2, G3). Each experiment was repeated three times, and the results were averaged three times. Table 1 displays the average experimental results for gas hydration in the SDS and NiMnGa-SDS systems. In addition, the Supporting Information Table S1 displays all the experimental results for gas hydration in the SDS and NiMnGa-SDS systems. Figure 2 depicts the temperature and pressure profiles from the end of gas injection to hydrate formation stabilization. The process of producing gas hydrates is divided into four stages: nucleation period (ab); rapid hydrate growth period (bc); slow hydrate growth period (cd); and stabilization period (de).

Particle Conc. (wt.%)	Exp. No.	Induction Time (min)	Gas Consumption (mmol/mol)	Hydration Reaction Time (min)	Gas Consumption Rate (mmol/mol/min)
0	G1-1	113.9	9.7	185.6	0.054
	G2-1	48.3	16.5	155.9	0.113
	G3-1	42.9	23.7	107.1	0.222
0.1	G1-2	3.4	11.9	92.2	0.135
	G2-2	8.9	16.6	76.4	0.221
	G3-2	5.8	26.2	74.0	0.360
1	G1-3	4.0	13.2	70.9	0.196
	G2-3	2.4	21.6	82.1	0.264
	G3-3	1.4	25.0	79.6	0.312
2	G1-4	5.3	10.8	48.0	0.229
	G2-4	2.6	21.4	59.0	0.363
	G3-4	3.0	27.1	67.0	0.410
3	G1-5	1.9	14.6	59.9	0.244
	G2-5	1.3	19.0	57.2	0.335
	G3-5	0.9	27.0	61.1	0.444

Table 1. The average results for the gas hydration kinetics experiment.



Figure 2. Temperature and pressure curves of hydrate formation in the G1-3 NiMnGa system.

4. Discussion

4.1. The Magnetic Properties of NiMnGa Alloy Particles

Figure 3 depicts the magnetization–temperature curves of NiMnGa alloy particles under 0 T and 0.09 T conditions. In the 0 T magnetic field, the magnetization is close to 0.4 emu/g. The difference of magnetization is about 30 emu/g at 0.09 T, which is much larger than that at 0 T, indicating that the increase in magnetic field can improve the magnetization of particles. At the same time, it also shows that NiMnGa alloy particles are magnetic at 0.09 T and can rotate in the solution with a 0.09 T magnetic field during the hydration reaction of natural gas to form micro/nanofluids.



Figure 3. The magnetization–temperature curves of NiMnGa particles: (**a**) magnetic fields in 0 T and 0.09 T; (**b**) the enlarged view in 0 T.

4.2. The Effect of NiMnGa Particle Concentration

4.2.1. The Induction Time

Induction time is a critical parameter in hydrate kinetics because it determines how quickly hydrate nucleation occurs. Figure 4 shows the variation of hydrate induction time in different gas samples with NiMnGa content. The induction time of all the gas samples is shortened greatly in the NiMnGa-SDS system as compared to the SDS system. With the increasing content of NiMnGa particles, the induction time further decreases slightly. The average induction time of the 0.1 wt.% NiMnGa-SDS system in three gas samples was 3.4, 8.88, 5.83 min, respectively; compared with the SDS system, the average induction time was shortened by about 97.0%, 81.6%, and 86.4%, respectively. It can be seen that the

addition of only 0.1 wt.% NiMnGa can shorten the induction time of hydrates significantly in different gas samples.



Figure 4. Induction time versus particle concentration curves.

Furthermore, in different concentrations of the NiMnGa-SDS system, the induction time of adding 3 wt.% NiMnGa was the shortest, which is 1.9, 1.3, and 0.9 min in the G1, G2, and G3 gas samples, respectively. These values of induction time are shortened by 98.3%, 97.2%, and 98.0% compared with the SDS system. As compared with SDS system, the small particle size of NiMnGa provides more nucleation sites. Meanwhile, particles collide at the gas–liquid interface to increase gas transfer due to Brownian motion [41]. Therefore, the induction time is shortened significantly by a small amount of NiMnGa particles.

On the other hand, in the SDS system, the induction time of the three gas hydrates decreases with the increase in CH_4 content; that is, the increase in CH_4 content contributes to the initial nucleation of hydrates in the absence of particles. However, in the NiMnGa-SDS system, the effect of CH_4 content on the induction time is not monotonous, which is different from the SDS system, but the three are concentrated between 0.9–9 min, indicating that NiMnGa particles are suitable for different CH_4 content gases in shortening the induction time.

4.2.2. The Gas Consumption

Figure 5 shows the dependence of gas consumption on particle content. The gas consumption of the NiMnGa-SDS system is greater than that of the SDS system and exhibits an increasing trend with the increase in particle concentration, although the effect of particle content is not identical for three gas samples. For example, the average gas consumption of the 0.1 wt.% NiMnGa-SDS system was 11.9, 16.6, and 26.2 mmol/mol, respectively, which was 22.4%, 0.5%, and 10.5% higher than that of the SDS system. In the G1 system, the gas consumption of the 3 wt.% NiMnGa-SDS system is the largest (14.6 mmol/mol), which is about 50.5% than that of the SDS system. With the increase in NiMnGa concentration, the metal surface that can provide hydrate formation increases. At the same time, NiMnGa particles move with the rotation of the gas—liquid interface and in the liquid phase, so that more CH_4 molecules can enter the liquid phase and begin to form on more metal surfaces, thereby increasing gas consumption.



Figure 5. Gas consumption versus particle concentration curves.

In addition, whether in the SDS system or the NiMnGa-SDS system, the gas consumption of the three gas hydrates increases with the increase in CH_4 content. It can also be seen in Figure 4 that in the G3 gas sample, the gas consumption of the SDS system alone is higher than that of all the systems in the G2 gas sample, and the G2 system is also higher than the G1 system. This indicates that although the gas consumption is increased by the NiMnGa particles with the concentration range used in the experiment, the CH_4 content is still the primary factor determining the amount of hydrate formation.

4.2.3. The Gas Consumption Rate

Figure 6a, b depicts the reaction time and gas consumption rate in various gas samples. In Figure 6a, all the hydrate reaction times of the NiMnGa-SDS system are less than 93 min, which is much shorter than those of the SDS system. It shows that the hydration reaction time can be shortened by NiMnGa particles effectively, and with the increase in NiMnGa particle concentration in the three gas samples, the reaction time of the hydrates decreases as a whole. Similar to the induction time, in the SDS system, the reaction time of the three gas hydrates decreases with the increase in methane content. However, in the NiMnGa-SDS system, the reaction time of all three gases is concentrated between 48–92 min, and the extent of shortening the reaction time of gas hydrates with low-concentration methane content (G1) is greater than that of gas hydrates with high-concentration methane content (G3), indicating that NiMnGa particles have a more significant effect on gas hydrates with lower-concentration methane content in shortening the reaction time.

Correspondingly, in Figure 6b, the gas consumption rate of the NiMnGa-SDS system is larger than that of the SDS system and exhibits an increasing trend with the increase in CH₄ concentration and particle concentration. The average gas consumption rate of the 0.1 wt.% NiMnGa-SDS system in the G3 gas sample is 0.360 mmol/mol/min, which is about 166.7% and 62.9% higher than the average gas consumption rate of the same NiMnGa concentration system in the G1 and G2 gas samples (0.135, 0.221 mmol/mol/min).



Figure 6. Curves of gas consumption rate with particle concentration: (**a**) reaction time; (**b**) gas consumption rate.

At the same time, adding a small amount of NiMnGa alloy particles has different degrees of improvement in the gas consumption rate among the three gas samples. The average gas consumption rates of the 0.1 wt.% NiMnGa-SDS system were 0.135, 0.221, and 0.36 mmol/mol/min, respectively, which were 150%, 95.6%, and 62.2% higher than those of the SDS system. In addition, the gas consumption rate for 3% NiMnGa in the G1 system is 0.244 mmol/mol/min, which is 351.9%, 80.7%, 24.5%, and 6.6% higher than that of 0 wt%, 0.1 wt.%, 1 wt.%, and 2 wt.% NiMnGa-SDS systems. This indicates that the higher concentration of NiMnGa is conducive to the rapid formation of hydrates in the experimental range of this paper. NiMnGa particles increase the gas–liquid reaction interface so that more CH₄ hydrates can grow at the same time. The gas consumption rate increases in a high speed during the rapid growth period of hydrates. The higher concentration of NiMnGa realizes the transport of more NiMnGa particles to the gas, and more CH₄ gas molecules enter the liquid phase continuously and participate in the formation of hydrates. Therefore, with the increase in NiMnGa concentration, the gas consumption rate has different degrees of upward trend.

4.3. Analysis of Gas Hydrate Enhancement by NiMnGa Micro/Nanofluids

4.3.1. The Effect of NiMnGa Particle Concentration on the Kinetics of the Gas Hydration Reaction

The magnetic NiMnGa particles are combined with SDS solution to form micro/ nanofluids by rotating magnetic field, to accelerate the kinetic process of the natural gas hydration reaction. Figure 7 shows the gas hydration process and the enhanced effect of gas hydration via different concentrations of NiMnGa micro/nanofluids. The NiMnGa-SDS system can effectively improve the hydrate kinetic conditions in different gas systems. The small particle size of NiMnGa micro/nanofluids can provide more reaction interfaces, increase hydrate nucleation and formation rates, increase heat exchange area between particles and fluid, and accelerate heat transfer during the hydration reaction. At the same time, due to Brownian motion, the particles collide at the gas–liquid interface to achieve gas transport purposes. The number of micro/nanoparticles per unit volume increases as the NiMnGa concentration increases, increasing the chance of inter-particle collision and increasing the efficiency of material transfer and heat transfer, while more NiMnGa particles can carry out gas transport at the gas–liquid interface and play a role in mass transfer.



Magnetic field direction Low concentration alloy particles High concentration alloy particles

Figure 7. Mechanism of CH₄ hydrate enhancement via different concentrations of NiMnGa.

In addition, NiMnGa phase transformation alloy is a thermoelastic martensitic transformation shape memory material [49]. When the hydrates are formed rapidly, NiMnGa particles can absorb part of the hydrate formation heat to reduce the ambient temperature appropriately [48], thereby promoting the hydrate formation process.

4.3.2. The Effect of External Magnetic Field on the Kinetics of Gas Hydration Reaction in NiMnGa Micro/Nanofluids

Combined with the magnetic properties of NiMnGa alloy, an experimental system of gas hydration reaction in a dynamic rotating magnetic field was built in this paper. The system is equipped with a vertical rotating magnetic field outside the titanium alloy high-pressure reactor, which drives NiMnGa alloy particles inside the reactor to flow in the liquid phase, achieving the strengthening of natural gas hydration reaction kinetics with NiMnGa alloy particles. The rotating magnetic fields can provide a magnetic field strength of 0~0.5 T. Due to the magnetic field, reducing the contact angle between the water and the solid surface, reducing the size and free energy of hydrate nucleation, and enhancing the movement of ions in the gaps between hydrate particles, the magnetic effect promoted the kinetics of natural gas hydration [37,38]. At the same time, the NiMnGa alloy particles used in the experiment, as measured in Section 4.1, exhibit magnetism at a magnetic field strength of 0.09 T and will rotate and flow with a 0.09 T magnetic field during the natural gas hydration reaction to form micro/nanofluids. This transforms the liquid phase into a liquid–solid two-phase suspension, changing the structure of a single liquid phase and promoting the energy transfer process within the micro/nanofluid. At the same time, the rotation of the magnetic field drives the alloy particles to play a strong stirring role in the liquid phase so that the NiMnGa alloy particles are uniformly dispersed and flowing in the base liquid, reducing the possibility of agglomeration. This also accelerates the gas transport of particles in the gas-liquid phase, allowing more gas molecules to enter the liquid phase to participate in the reaction. In the liquid phase, it accelerates the collision rate between particles and between particles and the gas-liquid phase, further promoting the transfer of gas-liquid substances, thus strengthening the dynamic process of natural gas hydration reaction.

5. Conclusions

The micro/nanofluids containing magnetic NiMnGa particles are used to improve the gas hydration process in this paper. Using this fluid system in an external rotating magnetic field, experiments on gas hydrate formation at various NiMnGa concentrations were carried out. The results show that NiMnGa micro/nanoparticles can promote the kinetic process of natural gas hydration reaction. At the same time, this promotion effect is further improved with the increase in NiMnGa concentration between 0.1–3 wt.%, and the promotion effect on the growth process of CH₄ hydrates is the best when the NiMnGa concentration is

3 wt.%. Compared with the SDS system in the G1 system, the induction time of the 3 wt.% NiMnGa system was shortened by 98.3%, the gas consumption was increased by 50.5%, and the gas consumption rate was increased by 351.9%. On the other hand, in different gas sample systems, the optimization of hydrate kinetic parameters becomes more obvious with the increase in CH_4 concentration in the gas samples. In the NiMnGa-SDS system, the effect of methane content on the induction time is not monotonous. The induction time of the three gas samples is shortened to 0.9–9 min, indicating that NiMnGa particles are suitable for different methane content gases in shortening the induction time. In addition, the effect of NiMnGa particles on gas hydrates with lower methane content is more obvious on shortening the reaction time. However, compared with the influence factors of NiMnGa particle content, methane content is still the primary factor determining the amount of hydrate formation. Therefore, the 3 wt.% NiMnGa system in the G3 gas sample has a strong effect on promoting the kinetic process of gas hydrates.

These findings not only provide a new type of accelerator for the formation of natural gas hydrates; they also open a new way for the application of NiMnGa alloy.

Supplementary Materials: The following supporting information can be downloaded at https://www. mdpi.com/article/10.3390/pr11113149/s1: Table S1: Experimental conditions and results for gas hydrates in different concentrations.

Author Contributions: Investigation, Z.Z. and M.E.; Project administration, B.Z. and Q.W. (Qiang Wu); Resources, Z.L. and H.M.; Supervision, L.L.; Writing—original draft, Z.Z. and X.W.; Writing—review and editing, Q.W. (Qiong Wu), Z.L. and L.L.; Funding acquisition, B.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (U21A20111, 51804105), the Fundamental Research Funds for the Central Universities (3072022TS1005), and the Fundamental Scientific Research Funds of Provincial Universities in Heilongjiang Province (Hkdcx201902).

Data Availability Statement: The research data is in the Supplementary Information.

Conflicts of Interest: The authors declare no conflict of interest.

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