Effective utilization of Coal Fly Ash (CFA): perspectives and opportunities in various industrial sectors and hydrocarbon extraction processes

Dmitry Klimov 1*

¹Oil and Gas Research Institute Russian Academy of Sciences (OGRI RAS), Gubkina st., 3, 119333, Moscow, Russia

Abstract. The global ecological problem associated with the efficient utilization of coal fly ash (CFA) requires serious attention and immediate measures for its resolution. According to studies, huge volumes of CFA are generated annually, but only 25% of the waste undergoes proper disposal. To overcome this alarming situation, a focus on increasing the utilization of CFA in various industrial sectors is necessary. The potential applications of coal ash in construction, electronics, resource recovery, wastewater treatment, agriculture, and other sectors are promising and require further research. Of particular interest is the use of CFA in industrial processes for hydrocarbon extraction. The physical, chemical, and mineralogical properties of ash, such as morphology, surface area, porosity, and chemical composition, make it suitable for various wellbore processes. Increasing the applicability of CFA in different industrial sectors and its use in hydrocarbon extraction processes would significantly enhance waste utilization levels and reduce negative impacts on the environment.

1 Introduction

The application of fly ash (CFA) is effectively facing a significant environmental problem that affects the ecosystem and leads to an increasing volume of waste. According to scientific studies [1, 2], the annual production of CFA worldwide is approximately 750 million tons, with only 25% of the ash being reused, leaving 75% of waste unused. Such a production versus utilization ratio indicates an imbalance [3], and serious efforts will be required to address this alarming situation.

To solve the global environmental problem associated with ash waste, the increased applicability of these waste materials in various industrial sectors plays a crucial role. Among these sectors, construction, electronics, resource recovery, mining and oil industries, wastewater treatment, chemical and pharmaceutical industries, agriculture, ceramics, and metallurgy can be highlighted [4]. However, further research on the physical

^{*} Corresponding author: seydem@mail.ru

[©] The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).

and chemical characteristics of waste from different sources is necessary for the more efficient utilization of these waste materials in order to inform stakeholders about the potential for increasing their utilization volumes.

The use of CFA waste as a raw material for industrial hydrocarbon extraction processes is considered a promising option for sustainable waste treatment. The physical, chemical, and mineralogical properties of these waste materials, such as their morphology, surface area, porosity, and chemical composition (including silica dioxide, aluminum oxide, iron oxide, titanium dioxide, etc.), make them suitable for various industrial processes [4].

Fly ash, formed during the combustion of pulverized coal in power plants, is a noncombustible inorganic solid substance. During combustion, mineral matter associated with coal is carried away by flue gases and forms ash particles containing significant amounts of chemical oxides, with aluminum oxide and silicon dioxide being the major components. On a global scale, coal mining companies annually produce about 750 million metric tons of such industrial waste [4].

The composition and properties of fly ash depend on the mineral composition of the burning coal. These minerals also undergo changes during combustion, burnout, and cooling. As a result of this complex process, particles with varying mineral contents are formed, including SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, BaO, SO₃, P₂O₅, and some other metal oxides [5].

A study conducted by Ghosal et al. [6] showed that over 90% of the coal ash sample contained particles with a diameter less than 8 μ m. Additionally, it was noted that a significant portion of the iron content was found in large ash particles. It is important to note that the composition of SiO₂ in large particles is higher than in smaller particles.

Depending on the amount of calcium oxide (CaO), fly ash can be classified as class F (with less than 20% CaO content) and class C (with more than 20% CaO content). Class C fly ash, obtained from the combustion of sub-bituminous or lignite coal, contains a significant amount of binding material and can be used in cementitious products. Class F fly ash, obtained from the processing of bituminous coal, does not contain cementitious material and does not harden in the presence of water [7].

Next, we will discuss the applicability of fly ash in various technologies and operations associated with the oil and gas industry and hydrocarbon extraction.

2 The application of fly ash in various areas of the oil and gas industry and hydrocarbon extraction

Every year, operations are carried out worldwide to combat water encroachment in oil wells [8]. Water production from oil reservoirs together with hydrocarbons from the rock formations can occur throughout the entire lifespan of the well. Water influx is closely related to coning and high-permeability zones. In order to successfully address the issue of well water encroachment, it is necessary to first accurately determine its nature and cause. Within the framework of enhanced oil recovery operations, there are various approaches to combating excessive water encroachment. Typically, they can be divided into two main groups: mechanical and chemical water shut-off methods. Mechanical methods are most effective for problems related to the wellbore, but can also be used in conjunction with chemical methods [9] became more acceptable in the industry and found widespread application compared to mechanical methods. Polymer gels are of great interest for use in oil production, including water shut-off treatments in oil wells [10]. A typical polymer gel consists of a water-soluble polymer and a crosslinking agent. A low-viscosity solution containing the polymer and crosslinking agent, often referred to as a gel former [11], can

transform into a rubber-like gel structure through a crosslinking reaction, where the polymer chains link together and form a three-dimensional structural network.

Today's widely used water-blocking gels mainly consist of polyacrylamides (PAM) or polysaccharides [9]. Despite advancements in technology in this field, most polymer gels have problems with optimal gelation time, insufficient viscoelasticity, and thermal stability, particularly at elevated temperatures (>80°C). Therefore, researchers and oil field operators have been actively investigating the incorporation of macro- and nanomaterials [9, 12-16] into polymer gel-forming solutions used for water-blocking to improve the aforementioned characteristics and enhance oil recovery.

The study by A.A. Adewunmi and colleagues [9] provides information on the gel formation process and dynamic rheological properties of polymer gels based on coal fly ash (CFA) obtained from polyacrylamide (PAM) cross-linked with polyethyleneimine (PEI). The choice of PEI as a cross-linking agent is due to its low toxicity and good water solubility. CFA contains numerous chemical oxides, with silicon oxide and aluminum oxide being the predominant ones. This is important as it is assumed that the high content of these chemical oxides in the ash positively affects the viscoelastic and gel-forming characteristics when it is incorporated into the primary PAM/PEI mixture. The study investigated the influence of different CFA additives on gel formation efficiency and viscoelasticity of pure PAM/PEI gel. Additionally, the impact of different concentrations of PAM and PEI on gel-forming and viscoelastic properties of composite PAM/PEI-ash gels was thoroughly examined. The active content of PAM and PEI was 20% and 33% by mass, respectively. All gel-forming solutions were prepared using a modeled formation water containing 2000 ppm NaCl. The researchers formed pure PAM/PEI gels without CFA, as well as composite PAM/PEI-CFA gels using various concentrations of CFA, PAM, and PEI. The percentage of CFA, PAM, and PEI ranged from 0.5-2%, 2.87-8.4%, and 0.3-1.04% by mass, respectively. NaCl solution was chosen for gel preparation as NaCl is a major component of salts present in formation water. The obtained composite gels with fly ash were evaluated at the normal formation temperature of 90°C [9].

The studies conducted by A.A. Adewunmi et al. [9] demonstrated that the addition of CFA increases the gelation time of PAM/PEI. Furthermore, increasing the concentrations of PAM and PEI leads to shorter gelation times for PAM/PEI-ash composites. The research revealed that the average gelation time is approximately 3120 hours, and a deep understanding of the reaction processes allows for accurate prediction of this time. Rheological property analysis showed that the elasticity modulus and viscosity modulus are significantly improved in composite PAM/PEI-CFA gels compared to pure PAM/PEI gel upon deformation. The enhancement in viscoelastic properties indicates effective interaction and the formation of a strong network of bonds between molecular chains. SEM microscopy confirms the consistency of gelation kinetics and rheological characteristics of the obtained compositions with ash additions. As a result, the experiment's authors strongly recommend limiting the amount of CFA to 1% by mass when creating polymer gels for water-blocking purposes.

Another frequently used chemical method for enhancing oil recovery associated with mobility control is polymer flooding. Due to the higher viscosity of polymers compared to water, the problem of finger formation arises, which has several ways of solution [17, 18]. As a result, the displacement of oil should significantly improve.

In the hydrocarbon industry, the most commonly used polymer is HPAM, or partially hydrolyzed polyacrylamide [19, 20]. Despite its drawbacks, this polymer has several advantages, however, some studies show that it is prone to degradation under the influence of several factors. In the oil industry, HPAM is used in various forms with different characteristics and concentrations. It is used for polymer flooding, as an additive to drilling

fluid, and as a gelling agent [21]. During the injection of HPAM, three main parameters to pay attention to are its concentration, degree of hydrolysis, and molecular weight [22].

In various studies, a wide range of polymer concentrations has been actively used [21]. These studies covered both low concentrations, ranging from 0.1 to 0.5% of the total mass, and higher concentrations ranging from 1 to 5% of the total mass of the polymer.

In the control of polymer mobility, there are several factors that can affect its degradation. Increasing the shear rate has a significant impact on polymer degradation [23]. Additionally, reservoir fluids, especially oxidizers, can influence the degradation of HPAM, especially at elevated temperatures [24, 25]. It is also worth noting that pore size can affect polymer degradation (ultra-small pore sizes can exhibit pseudoplastic behavior) [26].

The addition of a reinforcing agent significantly enhances the stability of the polymer. In this case, fly ash, generated by coal combustion at power plants, can serve as an effective and inexpensive reinforcement agent for polymer solutions [27]. The use of fly ash to strengthen the polymer is also considered important from an environmental perspective, as it significantly reduces the impact on the environment [28, 29].

Not enough research has been conducted on the possibility of using fly ash as a filler or reinforcing material for polymer products. There is a significant volume of research related to the use of fly ash as a filler or binding element in the formation of polymer hydrogels. From these studies, it can be concluded that hydrogels containing fly ash exhibit significant mechanical stability and rheological advantages compared to conventional hydrogels [30, 31, 32]. This indicates that fly ash can be a useful addition to hydrogels.

When developing a polymer injection project, one of the key factors that needs to be considered is the ease of injecting the polymer solution into the reservoir. If the polymer solution cannot be easily injected into the reservoir, it can lead to increased operation costs and an increased risk of reservoir fracturing [33]. There are multiple factors that influence the ease of polymer injection, including its properties such as rheology and concentration, as well as the injection pressure of the polymer and reservoir properties such as permeability and pore size [21]. The study conducted by S. Fakher et al. [21] aimed to perform a comprehensive experimental analysis of using fly ash for reinforcing HPAM polymer. The influence of polymer concentration, fly ash concentration, and injection rate on the ease of polymer injection were investigated.

When using a polymer solution with a polymer content of 0.1% by mass, the fly ash did not stabilize in the solution and precipitated, requiring an increased polymer concentration. When injecting the HPAM polymer solution with a fly ash content of 2% by mass, pipe plugging occurred, causing injection problems. The fly ash concentration did not have a significant influence on the average injection pressure. Therefore, as long as the fly ash is stably and uniformly distributed in the HPAM network, there should be no issues with pressure. The most stable combinations of HPAM with fly ash were found to be polymers with 0.5% and 1% by mass, mixed with 0.5% and 1% by mass of fly ash. The conclusions of the authors [21] suggest that the fly ash-incorporated HPAM polymer obtained through the experiments could be a better alternative to conventional HPAM for polymer injection operations aimed at enhancing oil recovery.

The heterogeneity of the reservoir is the main cause of high water production and low oil recovery, which leads to economic inefficiency of the process. To increase oil recovery, it is necessary to address permeability issues in order to achieve more uniform and effective displacement. Currently, research is being conducted on the creation of gels using preformed particles (PPG) that can eliminate reservoir heterogeneity and increase oil recovery. In a study conducted by K. Pereira et al. [34], the influence of coal fly ash (CFA) on hydrolyzed polyacrylamide (PHPA), cross-linked using polyethylenimine (PPG), was investigated to analyze changes in their thermal, rheological, and structural properties.

Polymeric gels are systems obtained from polymers that form a three-dimensional lattice structure and possess hydrophilic, soft, and semi-solid properties. These gels swell upon contact with water [34, 35]. One method of utilizing gel systems for conformance control is the use of compositions with preformed particles. These particles are easily prepared on the surface using a polymer and cross-linking agents before being injected into the target reservoir [36]. However, due to the fragility and softness of hydrogels, research efforts have been focused on developing new polymer hydrogels that are reinforced with fillers with improved mechanical properties, such as the addition of coal fly ash (CFA).

During the combustion of coal, the minerals associated with it are carried away as ash by the flue gases. It is because of this that the particles of this ash contain a considerable amount of chemical oxides, with alumina and silica being the main components. This property of fly ash contributes to the appearance of hydrogel properties [37, 38]. The use of fly ash in hydrogels created from cross-linked polyacrylamide (PAM) with polyethylenimine (PEI) hydrogels is mentioned in the literature as an inexpensive and environmentally beneficial approach [39, 40].

In the study by K. Pereira et al. [34], 30% hydrolyzed polyacrylamide (PHPA), also known as partially hydrolyzed polyacrylamide, was used. These polymers contain an acrylamide group (CONH₂) and an acrylic acid group (COOH) in their structure. PEI was used to cross-link these polymers, which has water solubility, low toxicity, and exhibits clear interaction through transamidation. Two different molecular weights of PHPA polymers were evaluated in the study, which were cross-linked using PEI and reinforced with fly ash (CFA). Then, to enable possible application in heterogeneous reservoirs, the optimal concentration of components was determined and the properties of gels with and without the addition of CFA were compared.

The initial investigation revealed the ideal composition with the highest Sidansky code (code I) and 1.0% weight content of PHPA and 1.0% weight content of PEI. X-ray phase analysis of the ash revealed characteristic diffraction peaks of minerals such as mullite and quartz. X-ray fluorescence analysis detected the presence of metals such as iron, silicon, potassium, calcium, and titanium, among others. Particle size measurement showed that their size ranged from 0.3 to 190.8 µm. Rheological analysis indicated that the solid properties increased with increasing CFA content. Gels with lower molecular weight PHPA showed the highest elastic modulus at a concentration of 0.5%, while gels with higher molecular weight PHPA showed a tendency of increasing elastic modulus up to 1.0%. Thermogravimetric analysis showed two stages of decomposition and increased thermal stability regardless of molecular weight. Systems with 1.0% CFA showed increased resistance by 271% compared to pure hydrogel. SEM revealed a well-distributed random filler morphology in the three-dimensional polymer network. Swelling experiments showed higher values for gels with higher molecular weight. Additionally, the presence of CFA decreased the swelling ability in all analyzed cases, indicating interaction between the components, leading to higher cross-linking density and swelling resistance [34].

The results of the study [34] indicate a significant improvement in the thermal and viscoelastic properties due to strong interactions between the polymer system and CFA with possible use of hydrogen bonds. The impact of CFA on hydrogels led to a significant enhancement of these properties, especially in terms of swelling ability, revealing new phenomena not previously reported in the literature. CFA systems exhibited a higher degree of swelling in brine compared to distilled water, indicating a protective effect of the filler on the interactions between PHPA anions and divalent cations of salt solutions. Such effects can be beneficial for blocking highly permeable wells. It is expected that these results will be utilized in technologies aimed at efficient oil recovery.

Successful foam flooding projects are accompanied by several technical and economic challenges. Among the economic issues, the availability of gas and compression costs, as

well as the cost of adsorbing surfactants on the rock surface, are particularly important [41]. The cost of adsorbed surfactant accounts for up to one-third of the oil production costs in the implementation of enhanced oil recovery (EOR) methods [42]. The technical problem lies in the instability of surfactants at high temperatures and high mineralization of reservoirs. When in contact with multivalent ions, anionic surfactants precipitate in saline water at temperatures above 100 °C. The introduction of additional surfactants, in addition to the main surfactant, can increase foam stability, thereby enhancing oil recovery efficiency [43]. However, such surfactants, known as foam boosters, are expensive and strongly adsorb onto rock surfaces. To overcome these limitations, the search for alternative co-surfactants to improve foamability and surfactant stability is required.

The study conducted by Eftekhari et al. [41] focused on the possibility of replacing expensive foam boosters with nanoparticles obtained from readily available fly ash using high-frequency ultrasonic grinding. The main goal of such research is to identify conditions such as nanoparticle concentration, surfactants, pH, temperature, salinity, and so on, that can provide a stable suspension with high efficiency and create a strong foam in a porous medium.

The role of surfactants in stabilizing the foam film can be explained through the balance between capillary pressure and disjoining pressure. Firstly, surfactants reduce the interfacial tension between gas and liquid, resulting in a decrease in capillary pressure (and thus drainage) and surface energy. Secondly, the presence of a surfactant at the gas-liquid interface increases surface charge, enhancing repulsive forces between gas-liquid interfaces [41].

Thus, fly ash of class F, containing a significant amount of amorphous aluminosilicate micro- and submicron-sized particles, can potentially be transformed into nanoparticles using an economical grinding and deagglomeration process. Large particles with high iron oxide content can be filtered out during grinding and deagglomeration to reduce the likelihood of precipitation of anionic surfactants [41].

There are several grinding technologies for reducing the particle size of fly ash. Grinding can be performed in both dry and wet conditions. Dry grinding typically produces a product with average particle sizes of 2 to 20 μ m, which can be further deagglomerated to particle sizes of around 1 μ m. However, wet grinding allows for even smaller particle sizes, not exceeding 100 nm [41].

Based on the research conducted by Eftekhari et al. [41], the following conclusions can be drawn. In core flooding experiments in Bentheimer sandstone, it was found that a foaming solution containing alpha-olefin sulfonate surfactants, as well as fly ash nanoparticles (nanofly ash), exhibited significantly greater stability compared to a conventional foam solution based solely on surfactants. Additionally, the amount of aqueous phase obtained from the mixing of nanofly ash with foam was much higher compared to the absence of nanofly ash. It was demonstrated that nanofly ash can be used for stabilizing surfactant foam in the presence of crude oil at high temperatures and pressures. Interestingly, volumetric foam containing only a small amount of nanofly ash exhibited higher stability in the presence of model oils. The study also noted that crude oil tends to form stable emulsions in water in the presence of nanofly ash.

It is important to note that CO_2 foams have long been used for enhanced oil recovery (EOR) and in carbon capture, utilization, and storage technologies. However, this approach to foam injection suffers from low storage efficiency and enhanced oil recovery due to foam instability. In the work of Q. Lv et al. [44], the geological storage of CO_2 and coal fly ash (CFA) was studied using Pickering foam to enhance oil recovery. The main goal was to develop a cost-effective method for enhancing oil recovery and storing greenhouse gases. In the experiments, improvements in the CO_2 /liquid interface were evaluated by measuring interfacial tension and interfacial viscoelastic modulus. The ability to control the oil

displacement profile and performance using CO₂-ash foam was also investigated using a heterogeneous packed sand model.

Research indicates [44] significant improvement in the stability of aqueous foam after the introduction of coal fly ash. The foam half-life with fly ash particles increased by more than 11 times compared to foam without particles. Increasing the concentration of CFA particles resulted in an increase in the dilatational viscoelastic modulus at the CO₂/foaming solution interface, indicating the transformation of reagents from liquid to solid state. Flooding experiments in heterogeneous porous media showed that using CO₂ foam with fly ash resulted in more efficient fluid recovery from low-permeability sandstone reservoirs. The use of CFA-stabilized foam improved oil recovery by approximately 28.3% compared to foam without particles. It was also found that the addition of ash particles to CO₂ foam enhances CO₂ trapping in heterogeneous porous media. Finally, ash stabilization of foam provides strong resistance to water erosion and can be used for CO₂ and ash storage.

Hydraulic fracturing technology, widely used in various regions, is a reliable way to enhance the productivity of low-permeability reservoirs. However, for increased effectiveness of this process, the introduction of nanoparticles prior to larger proppants placement becomes necessary. This approach successfully prevents fluid loss in the inner layers and significantly improves the conductivity of fractures and microfractures, thereby increasing production volume [4].

Proppants are strong spherical granules with diameters ranging from 0.25 to 2.5 mm, which prevent closure of hydraulic fractures under high pressure and provide the necessary productivity of oil or gas wells by creating a conductive channel in the formation. Proppants injected into different regions of the fracture can differ not only in their particle size distribution but also in density. Recently, a technology of massive hydraulic fracturing has emerged, which involves injecting lighter medium-strength proppants first, followed by higher-quality and high-strength proppants [45, 46].

A series of studies confirmed that the recovery of valuable proppants from CFA is a long-term strategic resource that increases oil and gas production [4]. A study conducted by Bose et al. [47] demonstrated that the use of CFA as nanoproppants enhances fracture conductivity, reduces water production, and seals microfractures. These nanoparticles have a significant impact on fracture conductivity and permeability, ranging from 27 to 33 mD.

Given the constant decline in reservoir pressure during oil and gas production, an increase in effective stress is observed, leading to the closure of fractures. The network of stimulated and natural fractures provides a pathway for hydrocarbon migration from the matrix to the well, an important aspect of successful exploitation of oil and gas from unconventional reservoirs. Due to its spherical shape and smaller size, fly ash is an attractive means of creating fractures with higher permeability [48]. At the same time, fly ash obtained from coal combustion is better suited for the formation of small-scale microfractures, hindering the penetration of conventional proppants [49].

In the course of research conducted by Kazakh scientists [45, 46], a mixture for proppant injection into the reservoir was developed, containing fly ash, bauxite, and kaolin as alumino-silicate raw materials. The proppant was composed of the following components: fly ash accounted for 75% of the total mass, kaolin - 15%, and bauxite - 10%. Analysis of the composition of the samples showed that the fly ash-based proppant contains more than 20 chemical elements, which was determined using energy-dispersive X-ray fluorescence spectrometry (EDXRF). Scientists [45, 46] have developed a technology based on the use of submicron particles from available materials - bauxite, quartz sand, kaolin, and white clay, as well as fly ash from thermal power plants (TPP), as proppants when using multi-stage hydraulic fracturing technologies. As a result of the study, the authors conclude that the use of fly ash with bauxite and other components in the

composition of proppants in multi-stage hydraulic fracturing is an effective tool to achieve good results.

The use of fly ash with a high content of volatile substances as a "microfracture agent" can enhance the impact on smaller fractures that are not sufficiently effectively opened by traditional methods. This opens up new possibilities for ensuring an efficient fracture opening process, especially in the context of the initial stage of inflow enhancement using hydraulic fracturing. In the framework of this inflow enhancement scheme, the "cushion for hydraulic fracturing" is one of the key components that usually does not contain fracture-opening fillers. Such a cushion creates a volume of fractures that are stimulated but not fully opened [50].

The revolutionary application of fly ash with a cushion in hydraulic fracturing can significantly improve the current fracture network, bypassing macrofractures and accumulating in the microfracture system, ultimately increasing the overall volume of the gas-oil reservoir [51]. Further research is needed to gain a deeper understanding of the mechanisms of its use as a source of macrofractures under certain conditions of active stress.

Approximately 23% of the total use of fly ash in the construction industry is accounted for by the production of various building materials, such as Portland cement, concrete, wall panels, roofing granules, paving materials, and bitumen fillers [52]. Fly ash has an incredibly low cost, superior mechanical strength, and ecological friendliness compared to Portland cement, which is subject to degradation. The technology of producing geopolymer cement using fly ash attracts attention, based on some interesting studies related to the creation of strong compositions for well cementing and sealing. This direction opens up new prospects for the effective use of fly ash in construction and well abandonment.

The production of Portland cement – the main binder in concrete material – has a significant negative impact on the environment, as it contributes to the emission of about 7% of the total volume of CO_2 into the atmosphere [53]. However, with the emergence of geopolymer concretes, successful alternative construction materials have been found that completely eliminate the use of Portland cement [54]. The problem of utilizing technological waste with cementitious properties becomes increasingly relevant, especially in the context of their partial or complete replacement of Portland cement in concrete mixtures. The use of fly ash from thermal power plants (TPP) and rice husk ash (RHA) to create innovative concrete mixtures appears to be an effective option [55].

One of the main components of geopolymer-based cementless concrete is alkaline liquids (a combination of NaOH and Na₂SiO₃ or KOH and K₂SiO₃), which stimulate its hardening, as well as fillers containing amorphous silica (SiO₂) and active aluminum oxides (Al₂O₃). In this regard, waste materials such as fly ash, rice husk ash, and blast furnace slag can be effectively used as components in the formulation. The mineral composition of the amorphous part of fly ash and rice husk ash mainly consists of melilite minerals, composed of gehlenite Ca₂Al₂SiO₇, akermanite Ca₂Mg(Si₂O₇), and merwinite Ca₃Mg(SiO₄)₂ [55].

During a research project conducted in 2000-2001, an extensive analysis of natural tests of geopolymer cement slurries for well cementing in Oklahoma was carried out. The main objective of the study was to investigate the possibility of using fly ash as an alternative cementing material [56, 57]. During the two-stage project, fly ash samples were collected from five coal-fired power plants in Oklahoma. Each sample underwent laboratory testing to determine the optimal composition of the slurry. Pumpability tests were also conducted to ensure the use of the cement slurry with flexible casing and tubing. The experiments showed that the slurry could easily flow through flexible tubing, allowing well operations to be carried out without a conventional drilling rig. The compressive strength of the best selected slurry compositions reached over 35 kg/cm², which met the minimum strength requirements for completing operations. Strength bond and gas permeability tests of the fly

ash slurry showed low permeability and high adhesive properties. Such a slurry provided a good contact surface with the casing, preventing fluid or gas migration. Ultimately, the tests confirmed that the fly ash slurry acted similarly to Class "H" cement and could be used for well cementing at depths of up to 1800 meters [56, 57].

The application of geopolymer materials in oil and gas wells faces a number of challenges that hinder their widespread use. The main ones are the fast setting time and temperature sensitivity. However, researchers, including S. Salehi et al. [58], found that fly ash-based geopolymers can provide a sufficiently long setting time with the right mixture composition. In another study [29], the analysis results of setting time for fly ash-based geopolymers were presented. Positive results showed that a setting time of over 300 minutes could be achieved at temperatures up to 80°C, and a comfortable setting time (several hours) could be achieved at temperatures up to 93°C without the use of retarders and superplasticizers.

The laboratory research results [58] show that fly ash-containing geopolymer samples have several advantages compared to Class "H" Portland cement samples. The first advantage is that geopolymer exhibits less shrinkage and lower water absorption. For example, after one day of curing at 90°C, the shrinkage of the geopolymer composition was about 2%, while for Portland cement, it was 4.6%. The second advantage is that fly ash-based geopolymers demonstrate an increase in strength over time. After two weeks of curing, the compressive strength of the geopolymer composition exceeded 420 kg/cm² under unrestricted compression. Moreover, it was noted that the rate of strength reduction with increasing temperature is lower for geopolymer compared to ordinary Portland cement. The third advantage is that fly ash-containing geopolymer samples show more plastic behavior and have a lower modulus of elasticity compared to ordinary cement samples after one day of curing. Additionally, hybrid cement composites with fly ash exhibit higher autogenous self-healing ability, allowing cracks to regenerate in case of structural damage.

The research conducted by S. Salehi et al. [58] also highlights the economic advantages of using fly ash-based geopolymer materials compared to Portland cement. According to their research, the cost of Class "F" fly ash is around \$20 per ton, while Portland cement costs over \$100 per ton without considering other additives. Furthermore, due to the increased strength of fly ash-containing mixes, fewer additional additives (such as silicates) are required, leading to additional economic benefits compared to Portland cement.

3 Conclusion

Therefore, summarizing the current review, the following key points can be highlighted on the investigated question.

• The majority of stitched polymer gels currently used for water shut-off treatment in wells do not always have suitable gelation times, insufficient viscoelastic properties, and thermal instability at elevated reservoir temperatures. Therefore, current research focuses on the development of water shut-off compositions with inclusion of macro- and nanomaterials to modify and improve the aforementioned characteristics during enhanced oil recovery processes. Stitched polymer gels based on coal fly ash can serve as a good additive in the component composition.

• The addition of fly ash and polymer materials in different proportions allows for the regulation of gelation time of the water shut-off composition, effectively predicting it. Rheological results from experiments show that the addition of fly ash to various composite gels significantly improves the elastic modulus and viscosity modulus. Scanning electron microscopy demonstrates the consistency of the gelation reaction kinetics and rheological properties of the obtained polymer compositions with fly ash.

• The most widely used polymer in the hydrocarbon industry (for polymer flooding, as an additive to drilling fluid) is partially hydrolyzed polyacrylamide (HPAM), which, despite its numerous advantages, is not always stable due to certain factors and reservoir conditions (concentrations of aggressive components in reservoir fluids, increasing shear rate, pore size, etc.). Therefore, the addition of reinforcing agent, in the form of fly ash, can significantly enhance the stability of the polymer. The most stable HPAM compositions with fly ash were found to be polymers with concentrations of 0.5 and 1 wt.%, mixed with 0.5 and 1 wt.% fly ash. The obtained HPAM polymers with fly ash can be a better alternative to the use of conventional HPAM compositions in polymer flooding operations for enhanced oil recovery.

• As part of addressing the permeability issue to enhance oil recovery, research on gel compositions with preformed particles (PPG) is actively conducted. Due to the brittleness of gel systems with preformed particles, the development of new polymer hydrogels reinforced with fillers with improved mechanical properties becomes relevant, for example, by adding coal fly ash (CFA). This leads to an increase in mechanical properties, thermal decomposition resistance, and a decrease in the swelling ability with increasing fly ash content in the gel system. Significant improvement in thermal and viscoelastic properties is indicated when fly ash is included in the composition. Hydrogel systems with fly ash showed a larger swelling effect in brine than in distilled water, which can be useful for blocking zones with higher permeability in wells.

• In the consideration of foam flooding projects in the enhanced oil recovery stage, the addition of an additional surfactant to the main foam-generating surfactant can lead to greater stability of the formed foam to oil, thereby increasing oil recovery. The possibility of replacing expensive foam boosters with inexpensive nanoparticles made from readily available fly ash using high-frequency ultrasonic milling is discussed. Nano fly ash can be used to stabilize foam in the presence of crude oil at high temperature and pressure. The volumetric foam containing a very small amount of nano fly ash particles exhibits higher stability in the presence of model oil samples, which also tend to form stable emulsions in water in the presence of nano fly ash.

• The widely used hydraulic fracturing technology improves productivity in lowpermeability reservoirs, and the use of nanoparticles before placing larger proppants helps prevent fluid imbibition into the reservoir, increase fracture and microfracture conductivity. Extracting valuable proppants from fly ash provides a long-term strategic resource that increases oil and gas recovery. Several studies on the use of CFA as nanopropants to enhance fracture conductivity and reduce water production and microfracture consolidation have demonstrated that fly ash nanoparticles show significant conductivity and permeability values in the range of 27 to 33 mD. The spherical shape and smaller size of fly ash make it attractive for use as a mechanism for wedging open higher permeability fractures. Fly ash can be used with a "fracturing cushion" during the initial inflow intensification process, enhancing the initially existing fracture network, bypassing macrofractures and settling into microfracture networks.

• Research on the geological storage of CO_2 and coal fly ash (CFA) using foam for enhanced oil recovery has been conducted. It has been noted that the addition of ash particles to the foam with CO_2 improves CO_2 capture in heterogeneous porous media. Foam stabilized with fly ash exhibits strong resistance to water erosion during CO_2 and ash storage.

• The use of fly ash as an additive in wellbore sealants and cementitious sealing composites shows great promise and yields promising results in experimental studies and pilot projects, offering several undeniable advantages over traditional solutions. Fly ash is increasingly being used as an active additive in the production of geopolymers, which appear to be highly advantageous due to their extremely low cost, superior mechanical

strength, and eco-friendliness compared to traditional Portland cement, which is prone to degradation.

4 Acknowledgments

The work was carried out within the framework of the state task of the Oil and Gas Research Institute of the Russian Academy of Sciences (OGRI RAS) on the topic number 122022800272-4 "Improvement of modeling methods, laboratory and field research for the development of new technologies for efficient and environmentally friendly hydrocarbon extraction in complex geological conditions".

References

- 1. J.C. Hower et al., International Journal of Coal Geology, 179, (2017).
- 2. R.S. Blissett, N.A. Rowson, Fuel, 97, (2012).
- 3. C. Wang, G. Xu, X. Gu, Y. Gao, P. Zhao, Ceramics International, 47 (2021).
- 4. R. Nsiah-Gyambibi et al., Int. J. Environ. Sci. Technol., 20 (2023).
- 5. B.G. Kutchko, A.G. Kim, Fuel, 85 (2006).
- 6. S. Ghosal, J.L. Ebert, S.A. Self, Fuel Processing Technology, 44 (1995).
- 7. O.E. Manz, Fuel, 78, (1999).
- B. Bailey, M. Crabtree, J. Tyrie, J. Elphick, F. Kuchuk, C. Romano et al., Oilfield Rev. 12(1) (2000).
- 9. A.A. Adewunmi, S. Ismail, A.S. Sultan et al., Korean J. Chem. Eng., 34 (2017).
- P. Albonico, G. Burrafato, A. Di Lullu, T.P. Lockhart, *Effective gelation-delaying* additives for Cr⁺³/polymer gels, SPE International Symposium on Oilfield Chemistry, SPE Journal, 25221, March 2–5 (1993).
- M. Simjoo, A.D. Koohi, M. Vafaie-Sefti, P.L.J. Zitha, *Water Shut-off in a Fractured System Using a Robust Polymer Gel*, SPE European Formation Damage Conference, SPE 122280, Netherlands, 27-29 May (2009).
- J. Aalaie, E. Vasheghani-Farahani, A. Rahmatpour, M.A. Semsarzadeh, Eur. Polym. J., 44 (2008).
- 13. T. Huang, P.M. Mcelfresh, *Compositions and methods for water shut-off in subterranean wells*, United States Pat. Number US 2004/0031611 A1 (2004).
- P. Patil, R. Kalgaonkar, *Environmentally acceptable compositions comprising* nanomaterials for plugging and sealing subterranean formations, SPE International Oilfield Nanotechnology Conference and Exhibition, SPE-154917-MS (2012).
- 15. P. Tongwa, R. Nygaard, B. Bai, J. Appl. Polym. Sci., 128 (2013)
- R. Zolfaghari, A.A. Katbab, J. Nabavizadeh, R.Y. Tabasi, M.H. Nejad, J. Appl. Polym. Sci., 100 (2006).
- 17. B. Al-Shakry, B.S. Shiran, T. Skauge, A. Skauge, *Enhanced Oil Recovery by Polymer Flooding: Optimizing Polymer Injectivity*, Soc Pet Eng, **SPE-192437-MS** (2018).
- B. Al-Shakry, B. Shaker Shiran, T. Skauge, A. Skauge, *Polymer Injectivity: Influence of Permeability in the Flow of EOR Polymers in Porous Media*, SPE EuropEC featured at 81st EAGE Conference and Exhibition, London, England, UK, SPE-195495-MS (2019).
- 19. R.S. Seright, SPE Journal, 22 (01), SPE-179543-PA (2017).

- 20. H. Koh, V.B. Lee, G.A. Pope, SPE Journal, 23 (01), SPE-179683-PA (2018).
- 21. S. Fakher, M. Ahdaya, A. Imqam, Fuel 260, 116310 (2020).
- 22. S. Fakher, B.A. Bai, A Newly Developed Mathematical Model to Predict Hydrolyzed Polyacrylamide Crosslinked Polymer Gel Plugging Efficiency in Fractures and High Permeability Features, SPE, **191180-MS** (2018).
- 23. X. Xin et al., Polymers, 10, 857 (2018).
- 24. W. Luo, S. Xu, F. Torabi, *Chemical Degradation of HPAM by Oxidization in Produced Water: Experimental Study*, SPE, SPE-163751-MS (2013).
- 25. R.S. Seright, I. Skjevrak, *Effect of dissolved iron and oxygen on stability of HPAM polymers*, SPE Improved Oil Recovery Symposium, SPE, **169030** (2014).
- 26. R.S. Seright, M. Seheult, T. Talashek, *Injectivity Characteristics of EOR Polymers*, SPE Reservoir Evaluation & Engineering, **12** (2009).
- 27. M. Ahdaya, A. Imqam, Journal of Petroleum Science and Engineering, 176 (2019).
- S. Salehi, M.J. Khattak, N. Ali, H.R. Rizvi, Development of Geopolymer-based Cement Slurries with Enhanced Thickening Time, Compressive and Shear Bond Strength and Durability, IADC/SPE Drilling Conference and Exhibition, SPE-178793-MS (2016).
- 29. S. Salehi, N. Ali, M.J. Khattak, H. Rizvi, *Geopolymer Composites as Efficient and Economical Plugging Materials in Peanuts Price Oil Market*, SPE Annual Technical Conference and Exhibition, Dubai, UAE, **SPE-181426-MS** (2016).
- 30. K. Fukui et al., Journal of Environmental Management, 90 (2009).
- K. Fukui, N. Arimitsu, K. Jikihara, T. Yamamoto, H. Yoshida, Journal of Hazardous Materials, 168, (2009).
- 32. L. Jiang, P. Liu, ACS Sustainable Chem. Eng., 2 (2014).
- 33. M. Lotfollahi et al., *Mechanistic Simulation of Polymer Injectivity in Field Tests*, SPE Journal, **21(04)** (2016).
- K.A.B. Pereira, K.A.B. Pereira, P.F. Oliveira, C.R.E. Mansur, J. Appl. Polym. Sci, 137, 49423 (2020).
- H.J. Rathod, D.P. Mehta, International Journal of Pharmaceutical Sciences, 1(1) (2015).
- Z. Zhang, L. Wang, J. Wang, X. Jiang, X. Li, Z. Hu, Y. Ji, X. Wu, C. Chen, Advanced Materials, 24(11) (2012).
- 37. Q. Jiang, X. Wang, Y. Zhu, D. Hui, Y. Qiu, Compos. Part B Eng., 56 (2014).
- 38. Y. Wang, R.S. Seright, *Correlating Gel Rheology with Behavior during Extrusion through Fractures*, SPE, **SPE-99462-MS** (2006).
- R. Singh, V. Mahto, H. Vuthaluru, Journal of Petroleum Science and Engineering, 165 (2018).
- 40. A.A. Adewunmi et al., Journal of Petroleum Science and Engineering, 157 (2017).
- 41. A.A. Eftekhari, R. Krastev, R. Farajzadeh, Ind. Eng. Chem. Res., 54 (2015).
- L.L. Wesson, J.H. *Harwell, Surfactant adsorption in porous media*, Surfactants: Fundamentals and Applications in the Petroleum Industry, Cambridge University Press (2000).
- R.F. Li, G.J. Hirasaki, C.A. Miller, S.K. Masalmeh, Wettability Wettability Alteration and Foam Mobility Control in a Layered 2-D Heterogeneous System, SPE International Symposium on Oilfield Chemistry, SPE-141462-MS (2011).

- 44. Q. Lv, T. Zhou, X. Zhang, X. Guo, Z. Dong, *Storage of CO2 and Coal Fly Ash using Pickering Foam for Enhanced Oil Recovery*, SPE International Conference on Oilfield Chemistry, **SPE-204330-MS** (2021).
- 45. A.K. Shokanov, A.A. Kyrykbayeva, B.T. Suleimenov, Neft' i gaz, 6 (132) (2022)
- A. Shokanov, B. Suleimenov, E. Smikhan, Bulletin of Shakarim University. Technical Sciences, 4(92) (2020)
- 47. C.C. Bose, B. Fairchild, T. Jones, A. Gul, R.B. Ghahfarokhi, Journal of Natural Gas Science and Engineering, **27** (2015).
- R. Snellings, G. Mertens, J. Elsen, Reviews in Mineralogy and Geochemistry, 74(1) (2012).
- 49. T.L. Robl, A.E. Oberlink, *Proppant for use in hydraulic fracturing to stimulate a well*, [Electronic resource]:https://uknowledge.uky.edu/cgi/viewcontent.cgi?article=1056&c ontext=caer_patents (Accessed: October 24, 2023) (2019).
- 50. R. Manchanda, *A general poro-elastic model for pad-scale fracturing of horizontal wells*, Doctoral dissertation (2015).
- 51. E. Ghanbari, H. Dehghanpour, Fuel, 163 (2016).
- 52. D.J. Tenenbaum, Environ Health Perspect, 117(11) (2009).
- M.A. Goncharova, N.A. Matchenko, Scientific research: from theory to practice: Proceedings of the V International Scientific and Practical Conference, Vol. 2, 4 (5) (2015).
- 54. A.G. Dudnikov, M.S. Dudnikova, A. Reggiani, Geopolymer concrete and its application, Stroitel'nye materialy, oborudovanie, tekhnologii XXI veka, **1-2** (2018).
- 55. T. Van Lam, B.I. Bulgakov, O.V. Alexandrova, *Possibility of using fly ash and rice husk ash to produce geopolymer concrete*, Innovations and modeling in building materials science and land management: Proceedings of the V International Scientific and Technical Conference, Tver (2021).
- 56. Working Document of the NPC North American Resource Development Study, Paper № 2-25. Plugging and abandonment of oil and gas wells, Prepared by the Technology Subgroup of the Operations & Environment Task Group, [Electronic resource]: <u>https://www.npc.org/Prudent_Development-Topic_Papers/2-</u> <u>25_Well_Plugging_and_Abandonment_Paper.pdf</u> (Accessed: October 24, 2023) (2011).
- S.N. Shah, Y. Jeong, Development of an Environmentally Friendly and Economical Process for Plugging Abandoned Wells, Proceedings of the 10th Integrated Petroleum Environmental Conference, Houston, TX, November 11-14 (2003).
- S. Salehi, C.P. Ezeakacha, M.J. Khattak, *Geopolymer Cements: How Can You Plug and Abandon a Well with New Class of Cheap Efficient Sealing Materials*, SPE Oklahoma City Oil and Gas Symposium, SPE-185106-MS (2017).