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Supervisor:
Associate Professor Borivoje Pašić, PhD

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Rudarsko-geološko-naftni fakultet

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UTJECAJ KORE MANDARINE NA SVOJSTVA ISPLAKE NA BAZI VODE I STABILNOST KANALA BUŠOTINE

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Zahvale

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ABSTRACT

In recent period, researchers have started conducting laboratory research to determine whether different types of biodegradable food waste can be used as additives in water-based muds (drilling fluids). Correctly designed composition of the mud is extremely important for the successful construction of the wellbore, since mud is complex fluid whose composition and properties affect the efficiency of drilling process. Therefore, any new type of additive must be researched in detail in relation to all the necessary properties that must be obtained during drilling operations. Wasted drilling mud and associated waste generated during drilling operations represents one of largest waste volumes accumulated during exploration and production projects in oil and gas industry, so this kind of research can have considerably positive results for the environment. Among the analyzed types of biodegradable waste, there is some data on the use of mandarin peel for these purposes, and due to the considerable annual production of this type of fruit in Croatia, it was decided that detailed laboratory research will be carried out on this type of biodegradable waste.

By adding dried, grinded and sieved mandarin peel powder, in the water-based drilling mud, it was tested how this additive affects the mud filtration properties, rheological properties and the wellbore stability. Drilling muds that have a certain concentration of mandarin peel powder in their composition were compared with base mud which consists of water, bentonite and sodium hydroxide (NaOH). In addition to studying the influence of the concentration of mandarin peel powder, the influence of different particle sizes divided into two groups, particles smaller than 0.1 mm and particles between 0.10 mm and 0.16 mm in size, was also researched. The selected concentrations in the mud samples varied from 0.5% to 2% by the volume of water, since it was concluded during preliminary laboratory test phase that a concentration higher than 2% leads to a significant increase in plastic viscosity of the tested muds.

On the basis of the conducted laboratory tests and the analysis of the results, useful insights were obtained on the effect of mandarin peel on the observed mud properties. Results show that mandarin peel have positive effect on mud filtration, since every mud sample with added mandarin peel powder showed decrease of filtrate volume. An exceptionally positive influence of mandarin peel powder was also observed in data obtained after swelling of pellets that have a clay component in their composition, when pellet is in contact with mud to which this eco-friendly additive is added. Laboratory tests showed significant swelling reduction, and this correlates well with results of filtration measurements which is essential to

prove the improvement of the wellbore stability. The rheological properties of mud samples that are containing mandarin peel were not decreased but also did not significantly increase observed properties. Rheological parameters show increase and remain within acceptable limits up to concentration of 1.5% of mandarin peel powder by volume of water. Because of this data set, the recommended concentration of this additive should be kept in the range of 1.0% to 1.5%, and at those concentrations observed additive has a significant positive effect on the filtration properties and wellbore stability as well as maintaining stable rheological properties at the same time. Considering the particle size used for laboratory research of mentioned mud properties, it can be concluded that slightly better results were obtained with larger particles between 0.10 mm and 0.16 mm but both sizes provide satisfactory water-based drilling mud properties. Also, by conducting laboratory tests of temperature stability, it can be concluded that water-based drilling mud with added mandarin peel powder is stable even after exposing the water-based drilling mud to temperatures up to 133 °C.

PROŠIRENI SAŽETAK

Mnogi komercijalno dostupni aditivi spadaju u kategoriju nerazgradivih i ekološki opasnih materijala te postoji potreba za pronalaženjem i stvaranjem novih ekološki prihvatljivih aditiva koji osiguravaju postizanje svih potrebnih svojstava isplake kao i komercijalno dostupni aditivi, ali uz minimalan utjecaj na okoliš. Stoga se posljednjih nekoliko godina aktivno provode mnoga istraživanja o mogućnostima primjene otpada od hrane i drugih vrsta biorazgradivog otpada u pripremi isplaka na bazi vode. Budući da su preliminarna ispitivanja pokazala pozitivan utjecaj praha kore mandarine na različita svojstva isplake na bazi vode, te uzevši u obzir razinu godišnje proizvodnje mandarina u Republici Hrvatskoj (40.580 tona u 2021. godini), korisno je detaljnije istražiti može li se otpad koji nastaje konzumacijom ovog voća iskoristiti u naftnoj industriji, odnosno za pripremu bušotinskih fluida.

Ciljevi i hipoteze

Ciljevi ovog rada su utvrditi primjenjivost koncepta kružne ekonomije u tehnologiji bušenja korištenjem otpadnog materijala (kore mandarine) u pripremi isplake te odabrati koncentraciju i veličinu čestica praha kore mandarine čija će primjena poboljšati reološka i filtacijska svojstva isplake, smanjiti bubrenje glinovitih stijena i posljedično povećati stabilnost kanala bušotine. Ciljevi su bazirani na tri hipoteze: (i) dodavanjem praha kore mandarine u isplaku na bazi vode poboljšat će se njena filtracijska i reološka svojstva, (ii) dodavanjem praha kore mandarine smanjit će se bubrenje glinovitih stijena i poboljšati stabilnost kanala bušotine i (iii) prah kore mandarine smanjit će toksičnost isplake.

Znanstveni doprinos

Rezultati ovog istraživanja donose uvid u odabir koncentracije i veličine čestica praha kore mandarine s ciljem optimiranja svojstava isplake i povećanja stabilnosti kanala bušotine u različitim bušotinskim uvjetima. Na temelju provedenih ispitivanja moguće je pojasniti mehanizam temeljem kojeg čestice praha kore mandarine djeluju na svojstva isplake i povećanje stabilnosti kanala bušotine te potvrditi primjenjivosti koncepta kružne ekonomije u području istraživanja ugljikovodika.

Metode i postupci

U svrhu definiranja utjecaja praha kore mandarine na odabrana fizikalna svojstva isplake na bazi vode provedena su detaljna laboratorijska ispitivanja prema standardima API 13A i 13B-1. Sukladno navedenim standardima za istraživanje utjecaja ovog biorazgradivog aditiva na bubrenje stijene korišteni su umjetno stvoreni uzorci stijene (peleti), a njihovo bubrenje ispitano je uređajem za mjerenje bubrenja (engl. *Dynamic Linear Swell Meter*). Laboratorijsko ispitivanje filtracije kroz keramičke diskove različite propusnosti u uvjetima povišenog tlaka i temperature provedeno je na uređaju za određivanje sposobnosti isplake da stvori premoštenje na licu formacije (propusnom mediju) (engl. *Permeability Plugging Tester (PPT)*). Primjenom skenirajućeg elektronskog mikroskopa (SEM) dobivene su SEM snimke površine isplačnog obloga kako bi se utvrdio mehanizam temeljem kojeg čestice praha kore mandarine čepe pore i tako smanjuju vrijednosti filtracije. Reološka svojstva (plastična viskoznost, naprezanje pri pokretanju i čvrstoća gelova) određena su Fann viskozimetrom model 35A.

Rezultati i zaključci

Kako bi se što bolje istražio utjecaj praha kore mandarine na filtracijska i reološka svojstva te smanjenje bubrenja umjetnih uzoraka glinovitih stijena (peleta), za usporedbu je odabrana isplaka na bazi bentonita (osnovna isplaka). Rezultati dobiveni laboratorijskim ispitivanjima osnovne isplake uspoređeni su s rezultatima ispitivanja osam isplaka na bazi vode u čijem se sastavu nalazila različita koncentracija praha kore mandarine različitih veličina čestica. Od toga su četiri isplake (oznake A1, A2, A3 i A4) sadržavale prah kore mandarine s česticama manjim od 0,10 mm, dok su preostale četiri isplake (oznake B1, B2, B3 i B4) sadržavale prah kore mandarine s veličinama čestica između 0,10 i 0,16 mm. Prah kore mandarine dodan je u sastav isplake u četiri različite koncentracije: 0,5% (oznake A1 i B1), 1% (oznake A2 i B2), 1,5% (oznake A3 i B3) i 2% (oznake A4 i B4) na volumen vode korištene za pripremu isplake. Laboratorijskim ispitivanjima utvrđeno je da prah kore mandarine značajno smanjuje API filtraciju isplake već pri koncentraciji praha kore mandarine od 0,5%, ali je dodatkom 2% praha kore mandarine volumen filtrata smanjen čak za 44% u odnosu na osnovnu isplaku. U uvjetima povišenog tlaka i temperature (34,5 bar i 88 °C) dobiveni su još bolji rezultati, odnosno zabilježeno je smanjenje volumena filtrata za čak 61,5% (isplaka B4) u odnosu na osnovnu isplaku. Vrijedno saznanje vezano za filtracijska svojstva je da prah kore mandarine uspijeva dodatno smanjiti filtraciju isplake na bazi vode koja sadrži PAC R (komercijalni aditiv za smanjenje filtracije) do čak 46,2%. Metodom 16-

satnog starenja isplake na povišenim temperaturama (75 °C, 100 °C, 125 °C, 133 °C, 142 °C i 150 °C) ispitivana je i temperaturna stabilnost isplake na bazi vode u koje je dodan prah kore mandarine te je dokazano da ovaj materijal ima pozitivan utjecaj na filtracijska svojstva isplake i nakon njenog dugotrajnog izlaganja temperaturama do 133 °C.

Vrijednosti reoloških svojstava isplaka na bazi vode koje, u različitim koncentracijama i veličinama čestica, sadrže prah kore mandarine nisu smanjene, ali nisu niti značajno povećane što znači da dodavanje ovog materijala ne narušava navedena svojstva isplake. Općenito, dodavanjem praha kore mandarine (obje ispitivane skupine veličina čestica) vrijednosti reoloških svojstava ispitivanih isplaka se povećavaju, ali ostaju u prihvatljivim granicama do koncentracije od 1,5% praha kore mandarine na volumen vode. Pri koncentraciji od 2% praha kore mandarine (veličine čestica između 0,10 i 0,16 mm) značajno se povećavaju vrijednosti reoloških parametara. Korištenje isplake na bazi vode s 2% praha kore mandarine u bušotinskim uvjetima rezultiralo bi povećanim gubitkom tlaka pa se može zaključiti da je prihvatljiva koncentracija praha kore mandarine do maksimalno 1,5% na volumen vode za testirane veličine čestica.

Iznimno pozitivan utjecaj praha kore mandarine uočen je i kod ispitivanja bubrenja umjetnih uzoraka stijene (peleta) koje u svom sastavu imaju glinovitu komponentu. Smanjenje bubrenja peleta u isplakama koje sadrže prah kore mandarine, u usporedbi s bubrenjem u osnovnoj isplaci, bilo je vidljivo već nakon dodavanja 0,5% ovog aditiva na volumen vode za pripremu isplake. Međutim, najbolji rezultati, odnosno najmanje bubrenje peleta, zabilježeno je u isplakama na bazi vode koje su sadržavale 2% praha kore mandarine. Smanjenje bubrenja peleta nakon 24-satnog ispitivanja bilo je do 45% u sobnim uvjetima, a do 48,6% na temperaturi od 90 °C. Jednako kao i za provedena ispitivanja filtracijskih svojstava, još bolji rezultati zabilježeni su u uvjetima povišene temperature u odnosu na sobne uvjete, a čestice veličine između 0,10 mm i 0,16 mm imaju nešto bolji učinak na smanjenje bubrenja, tako da ovi rezultati dobro koreliraju s rezultatima mjerenja filtracije što je bitno za procjenu poboljšanja stabilnosti kanala bušotine.

Usporedbom zbirnih rezultata ispitivanja utjecaja praha kore mandarine na sva promatrana svojstva isplake na bazi vode, može se zaključiti da su nešto bolji rezultati dobiveni s većim česticama praha kore mandarine (između 0,10 mm i 0,16 mm), iako se s obje veličine dobivaju zadovoljavajuća svojstva ispitivanih isplaka. Dodavanjem praha kore mandarine u koncentraciji od 1,0% do 1,5% na volumen vode za pripremu isplake, bez obzira na veličinu čestica, dobiveni su iznimno pozitivni rezultati vezani uz filtracijska svojstva i stabilnost kanala bušotine. Navedena koncentracija može se smatrati optimalnom za pripremu isplake na bazi vode koja će se koristiti za izradu kvalitetnog kanala bušotine. Međutim, osim očitog pozitivnog utjecaja na filtracijska i reološka svojstva isplake te povećanje stabilnosti kanala bušotine, primjenom praha kore mandarine u isplakama na bazi vode doprinosi se i konceptu kružne ekonomije u tehnologiji bušenja obzirom da iz otpadnog materijala nastaje koristan aditiv za dizajn isplake.

KEYWORDS

Water-based drilling mud

Mandarin peel powder

Filtration properties

Rheological properties

Wellbore stability

KLJUČNE RIJEČI

Isplaka na bazi vode

Prah kore mandarine

Filtracijska svojstva isplake

Reološka svojstva isplake

Stabilnost kanala bušotine

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1. INTRODUCTION

Drilling mud is a fluid used during the drilling of oil, gas and geothermal wells, and consists of a liquid base (water, oil or synthetic organic compounds) to which various additives are purposely added to adjust its properties. By circulating through the well, the mud ensures the continuous removal of drilled cuttings from well to surface, pressure control, the lubrication of the drilling tools, maintenance of the wellbore stability while drilling through various types of formations, etc. **(Pašić et al., 2007; Pašić et al., 2020; Ghaderi et al., 2020; Medhi et al., 2020; Ikram et al., 2021; Li et al., 2021)**. Correctly determined composition of the mud is extremely important for the successful construction of the wellbore, since mud is complex fluid whose composition and properties affect the efficiency of drilling operations and mud should meet all necessary conditions that are specific to each well **(Gaurina-Međimurec et al., 2000a)**. Considering the composition of the mud according to the liquid base, oil-based drilling mud is usually preferred for high pressure and high temperature conditions, and for the drilling through highly reactive shale formation. The main advantages of using this type of mud are higher rate of penetration (ROP), smaller possibility of mud loss during circulation, greater wellbore stability while drilling formations containing a high proportion of water sensitive clay, and reduction of torque and drag **(Gaurina-Međimurec, 1998; Mowrey and Cameron, 2006; Ramasamy and Amanullah, 2019; Mao et al., 2020)**. Despite all the positive properties, due to high toxicity the use of this type of mud is limited because of increasingly strict legal acts in the field of environmental protection. Another significant problem related to oil-based drilling mud is the high price **(Liu et al., 2019)**, especially compared to water-based mud. Cost is even greater during offshore drilling operations since it is legally prohibited to discharge oil-based mud and drilled cuttings into the sea, which means that transportation of this type of mud to land is necessary to ensure proper disposal.

As a result, water-based mud is most often used for drilling oil and gas wells. This type of mud mainly consists of fresh or salt water (90-95%), with the addition of polymers, clay minerals and various chemical additives **(Khodja et al., 2010)**. During drilling operations, significant amount of waste is generated and must be properly processed and disposed. Used mud represents the second largest volume of waste generated during the exploration and production projects **(Haut et al., 2007; Gaurina-Međimurec et al., 2020)**, and many commercially available water-based mud additives fall into the category of non-degradable and environmentally hazardous materials **(Zheng et al., 2020)**. Along with environmental protection, the disposal of generated waste presents a significant cost, which leads to a logical conclusion that reducing the amount of hazardous waste to the lowest possible value must be a priority. Considering the current situation, there is a need to find and create new environmentally friendly additives that ensure the achievement of all the necessary mud properties at the level of current commercial additives, but with a minimal impact on the environment **(Zhang et al., 2014)**. Therefore, many researchers are actively conducted on the use of food waste **(Haider et al., 2019)** and other types of biodegradable waste as additives that could be used for this purpose. On average, one person generates 65 kg of food waste per year, of which 25% are wasted vegetables, 24% wasted cereals and 12% wasted fruits **(Chen et al., 2020)**. According to data from the World Bank amount is even greater - 2.01 billion tons of municipal solid waste (0.74 kg per person per day), of which 44% is food and green waste **(Kaza et al., 2018; Amanullah, 2022)**. It is expected that by 2050, the annual amount of waste will grow to 3.40 billion tons **(Kaza et al., 2018)**, which encouraged researchers to think about the potential use of food waste to reduce its amount, and at the same time get usable products. With regard to the generally accepted trend of turning the industry towards a circular economy and reducing negative impact on the environment, it is important to explore possibility of applying those principles in the field of drilling, through the use of environmentally friendly additives in the preparation of water-based drilling mud.

1.1. Overview of research on the use of biodegradable waste in water-based drilling mud

In recent years, laboratory tests have begun to be conducted to determine whether different types of biodegradable food waste (mainly fruits and vegetables) can be used as additives in water-based muds. Most research is focused to research the possibility of using waste organic materials as additives for adjusting rheological and filtration properties.

According to the available literature, the authors examined a wide range of different types of biodegradable waste in order to determine their impact on mud properties, such as potato peel, palm leaves, grass, green olive seeds, mandarin peel **(Al-Hameedi et al., 2019a; Al-Hameedi et al., 2019b; Al-Hameedi et al., 2020a; Al-Hameedi et al., 2020b)**, chicken egg shells **(Al-Hameedi et al., 2020c)**, chicken egg and snail shells **(Onolemhemhen et al., 2019)**, saffron purple petals **(Ghaderi et al., 2020)**, banana peel, olive pulp, corn cob, pomegranate peel, peach pulp, soybean peel, sugar cane, henna, coconut shell **(Al-Saba et al., 2018)**, grapefruit peel **(Zhang et al, 2020)** and rice husk ash **(Yalman et al., 2021)**. Most of the research is focused primarily on identifying waste material as a potential additive and to get a more pronounced effect of an individual additive on the properties of the mud, usually a basic mud. These basic muds are mostly bentonite suspensions, usually with the addition of a small amount of NaOH, which regulates the pH value of the fluid. In these researches biodegradable waste was added in different concentrations (from 0.285% up to 16%), but in most cases concentrations up to 4% by volume of water have been used. After a detailed review of the literature, it can be determined that different authors obtained opposite results when examining the properties of water-based drilling mud after adding same type of biodegradable waste in same mud composition, which indicates that this area must be investigated in more detail. Also, most of the research refers to the possibility of using waste materials as additives only to adjust rheological and filtration properties in water-based mud. Since shale formations present 75% of all formations through which a well is drilled **(Pašić et al, 2007; Han et al., 2009; Song et al., 2017; Gholami et al., 2018; Darwesh et al., 2018)**, there is a need to research influence of eco-friendly additives on wellbore stability by using it in water-based mud. This type of research is extremely important to determine if this group of additives can successfully fulfill a wider range of tasks during drilling operations through formations containing water sensitive clay minerals, such as smectite. It is also important to note that the bulk of the research was carried out in room conditions, which means that there is a lot of space for more detailed laboratory tests of biodegradable waste in different mud compositions under conditions of elevated temperature and pressure. It is well known that the effect of pressure on drilling mud properties is important but not critical. However, the influence of temperature is extremely important due to the temperature instability of most water-based drilling muds at high temperatures because of degradation of many mud additives **(Allawi et al., 2019; Leusheva and Morenov, 2022)**.

Considering the level of mandarin production in the Republic of Croatia, which in 2021 was 40,580 tons **(Croatian Bureau of Statistics, 2022)**, and positive results obtained by laboratory tests of rheological properties and API filtration of mud **(Al-Hameedi et al., 2019b)**, the domestic oil and gas industry could be especially interested in using mandarin peel as an additive for regulation of certain mud properties.

1.2. Filtration properties

In the field of drilling fluids, filtration is defined as the process of extracting the liquid phase from the mud through a permeable medium (porous rock), under the impact of differential pressure, which is equal to the difference between wellbore pressure and pore pressure. At the same time, a mud cake, formed by solid particles present in the drilling mud, is created on the wellbore walls. In order for the mud cake to be considered high-quality, it must be thin, tough and with low permeability **(Yao et al., 2014; Al Jaber et al., 2021)**. If a high-quality mud cake can be created on the wellbore walls, the positive consequence is the prevention of further penetration of the mud filtrate into the rock, which makes the wellbore walls tighter and more stable. Mud filtration can be measured by the API filter press, HTHP (High Temperature and High Pressure) filter press or PPT (Permeability Plugging Tester) device. The API filter press (**Figure 1-1**) consists of a cell into which mud is poured and pressurized at 6.895 bar (100 psi) for 30 minutes. During this time period the volume of filtrate is extracted from the mud through filter paper (Whatman No.50) and collected in a laboratory beaker. The surface of the filter paper is 45.8 cm^2 (7.1 in^2). Filtration properties of the mud are determined according to the API RP 13B-1 standard **(American Petroleum Institute, 2003)**.

Figure 1-1. API filter press

The HTHP filter press consists of a cell into which mud is poured and high temperature is applied along with high pressure (temperature up to 260 °C, pressure up to 138 bar) where as a filter medium can be used filter paper (Whatman No.50) or ceramic discs (**Fann Instrument Company, 2014**). In order to compare values of API and HTHP filtration the filtrate volume obtained with HTHP filtration should be multiplied by 2 (OFI Testing Equipment, Inc., 2014), because the surface of filtration is 22.9 cm^2 (3.5 in^2), which it is twice as small as on API filter press. Filtration values can also be measured by using PPT device, which represents modification of standard HTHP filter press. PPT device is used for determining the drilling mud's ability to create bridging on the surface of permeable rock under conditions of high pressure and high temperature, which means that it is useful for evaluating the mud's ability to form a quality mud cake that will prevent further penetration of the filtrate through the filter medium. After a certain volume of mud is prepared, it is poured into the PPT cell in the first step. The required pressure is achieved by a pump which, acting on the bottom surface, pushes the mud through the ceramic disk (filter media) placed on the upper side of the cell. The filtrate is collected in a beaker after 7.5 and 30 minutes by releasing it from the device via a separate valve. Permeability Plugging Tester is shown in **Figure 1-2**.

Figure 1-2. Permeability Plugging Tester

The filtration area is 22.9 cm^2 (3.5 in^2), which is half the size of filter paper surface area used in API filter press cell, so filtrate volume must be multiplied by 2, and spurt loss (filtrate volume collected before forming a mud cake) can be calculated by using Equation 1-1 **(OFI Testing Equipment, 2015)**:

$$\text{Spurt loss} = 4 \cdot V_{7.5} - 2 \cdot V_{30} \tag{1-1}$$

- where:

$V_{7,5}$ – filtrate volume collected after 7.5 minutes, ml

V_{30} – filtrate volume collected after 30 minutes, ml

For this research, all mud samples were analysed by API filter press (room temperature, pressure of 6.895 bar) and Permeability Plugging Tester at 88°C and a differential pressure of 34.5 bar on a ceramic discs with permeabilities of 0.4 μm^2 (400 mD) and 0.75 μm^2 (750 mD).

1.3. Rheological properties

The rheological properties of the mud are important because they affect the removal of drilled cuttings from the bottom of the well to the surface, holding cuttings and weighting additives in suspension during the period of circulation interruption, cuttings release on the surface, resistance to mud flow, and an increase of wellbore pressure **(Gaurina-Međimurec et al., 2008)**. Rheological parameters include plastic viscosity, yield point and gels strength (10 seconds and 10 minutes). Plastic viscosity is a function of the friction between the solid particles in the mud, the amount of charge on these particles and the viscosity of the dispersed phase, and it can be defined as mud resistance to flow. As a result of high plastic viscosity values, the hydraulic effectiveness decreases, pressure surges and the occurrence of swabbing action is accelerated. Plastic viscosity values increases during drilling operations by increasing the proportion of solid particles **(Gomaa et al., 2020)**, such as barite or bentonite, or increase of drilled cuttings volume in drilling mud. Yield point is a function of force between solid particles in the drilling fluid and represents the capability of a drilling mud to remove the cuttings from the annular space of the wellbore. It can also be defined as a stress required to initiate mud circulation **(Murtaza et al., 2021)**, or initial flow resistance. Gel strength should be measured after 10 s and 10 min (during that period mud is in static condition), to show minimum required shear stress to initiate mud movement (10 s value) and thixotropic property of mud (10 min value).

The rheological properties of the mud (viscosity, yield point and gel strength (10-s and 10-min gel) are usually adjusted by adding clay (bentonite) or polymers (xanthan gum, guar gum, cellulose). Also, important factor for adjusting the composition of the mud also includes measuring pH value of the mud, since when the pH value increases, the rheological properties of the mud also increase. General rule is that pH value of mud should be between 8 and 10 **(Nickdel Teymoori and Ghasem Alaskari, 2007; Medhi et al., 2020; Ulyasheva et al., 2020)**, although some authors believe that the ideal range is from 9 to 10 for water-based mud **(Gamal et al., 2019; Koh et al., 2022)**.

In room conditions, rheological properties can be measured by Fann viscometer model 35A, shown on **Figure 1-3**, and to determine these values at elevated temperature device as OFITE Model 900 viscometer (**Figure 1-4**) can be used for test on elevated temperature up to 88 °C.

Figure 1-3. Fann viscometer model 35A

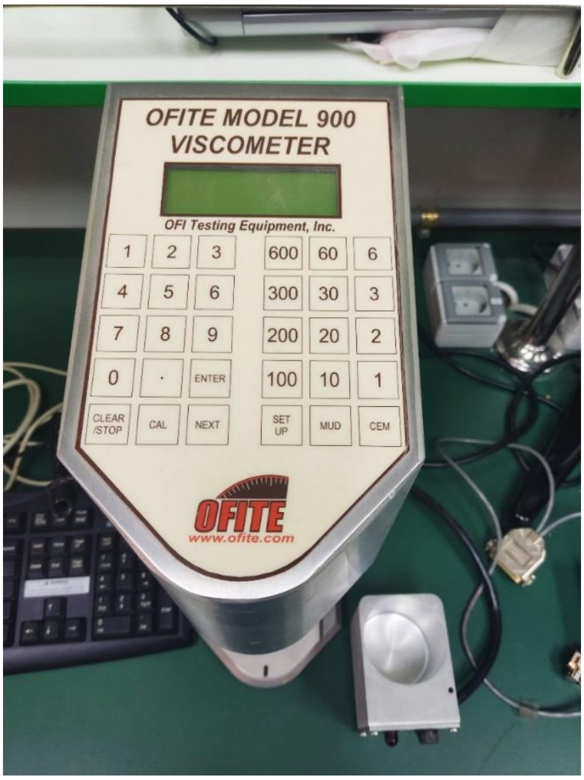

Figure 1-4. OFITE Model 900 viscometer

1.4. Wellbore stability

One of the most pronounced problems that can occur during drilling is related to the occurrence of wellbore instability, which can be defined as any unwanted change in the diameter of the well. The consequences of the problems related to wellbore stability can be different, and it is not unusual that requires expensive solutions that comes along with additional time to finish drilling operations. Approximately 30% of all possible unplanned costs during drilling operations is spent to solve the consequences of wellbore instability **(Muniz et al., 2005)**. In certain circumstances it can lead to loss of a wellbore section or the entire well. Problems related to wellbore instability became more pronounced with the increase of deep wells drilling, small diameter wells, multilateral wells, and drilling in underbalanced conditions **(van Oort et al., 1996)**. In practice, a whole series of problems that appear in well can be a consequence of the wellbore instability, such as poor cleaning of the well, poor cementation job, inability to perform logging measurements, problems when running out/down a drilling string or casing, etc. **(Labenski et al., 2003; Osuji et al., 2008; Qu et al., 2009)**. These are reasons for increased need to analyze wellbore instability during the planning phase of field development to keep project economics inside reasonable limit.

The causes of wellbore instability can be divided into two groups **(Gaurina-Međimurec, 1992; Pašić et al., 2007; Osuji et al., 2008)**:

- mechanical causes, and/or
- physico-chemical causes.

The mechanical causes of wellbore instability are the result of the mechanical properties of the underground formations through which drilling operations takes place, as well as changes in the state of stress on the wellbore walls, while the physico-chemical causes are the result of the interaction between the rock and mud. The mechanical causes of wellbore instability are related to the disruption of the existing state of stress in the formation because part of the volume of the rock is replaced with mud, and a new stress system is established on the wellbore walls. In addition, due to the contact between the rock which contain different water sensitive clay minerals (e.g. montmorillonite, kaolinite, illite and chlorite) and aqueous phase from the mud, the behavior of the formation depends primarily on the type of the present clay minerals and their tendency to hydration **(Karpiński and Szkodo, 2015)**, what is basic example of physico-chemical cause. This type of wellbore instability is usually associated with shale rocks due to their high clay mineral content and extremely low permeability **(Steiger, 1982; Bol et al., 1994; Ewy and Stankovich, 2002)**. Most often wellbore instability is a consequence of both groups of causes **(Ballard et al., 1994; Fink, 2011)**.

Water-based drilling muds are usually less expensive and more environmentally friendly, but they often have technical limitations that prevent their use in demanding drilling conditions, but one of biggest problem with the application of water-based mud is the inherent reactivity of water phase with clay minerals that are an integral part of formations like shales. Excessive shale hydration during drilling can lead to various problems beside wellbore stability, such as excessive mud viscosity, lower rate of penetration and bit balling **(May et al., 2020)**. In order to stabilize the shale formation, polymers such as acrylates, polyacrylates, acrylamides and polyacrylamides can be used, but most commonly used additives to prevent clay hydration are various types of salts such as KCl, NaCl, NH_4Cl or $CaCl_2$ **(Pašić et al., 2020)**. Also, reducing the filtration rate can effectively reduce the reaction of the mud (filtrate that penetrates in formation) with the rocks of the near-wellbore zone and consequently contribute to the wellbore stability.

In order to get a better insight into the influence of mandarin peel powder on the reduction of rock swelling, and thereby increasing of wellbore stability, artificial rock samples (pellets) containing a clay component were prepared as part of research for this doctoral thesis. The pellets consisted of bentonite as a swelling component and quartz as an inert component in a 1:1 ratio and were prepared by placing 6 g of each component in the compactor cell (**Figure 1-5**) and applying a pressure of 41.36 MPa (6000 psi) in duration of 30 minutes.

Figure 1-5. Compactor with two cells

After the compression time of 30 min in compactor cell, the bentonite–quartz pellets were removed from cell and placed in the Dynamic Linear Swell Meter (**Figure 1-6**), to determine their swelling in different muds. The swelling test for each pellet in the selected base drilling mud and muds that contained mandarin peel powder of different concentrations and particle sizes was run for 24 h.

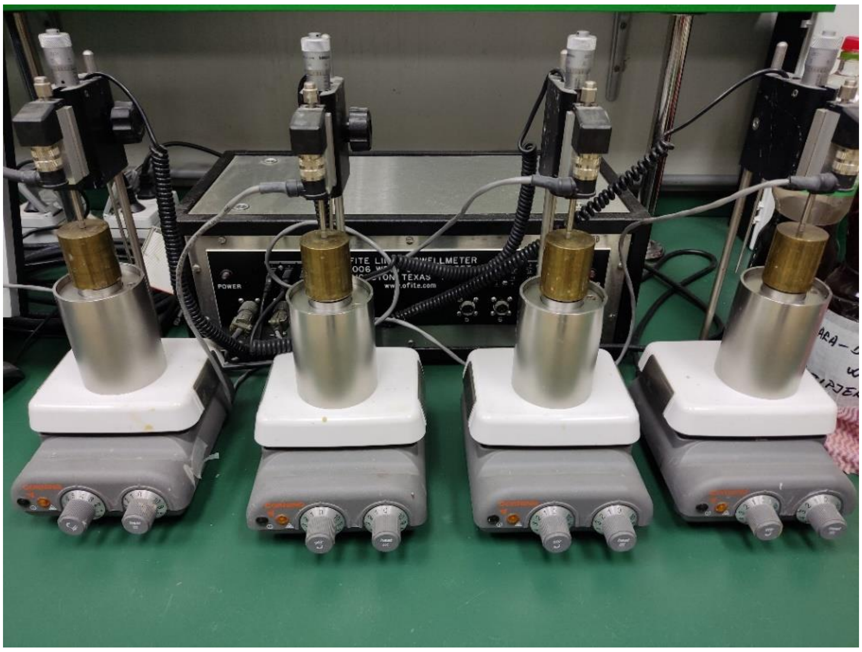

Figure 1-6. Dynamic Linear Swell Meter

1.5. Objectives and hypotheses of research

Objectives of this research were: (1) to determine the applicability of the concept of circular economy in drilling technology using waste material (mandarin peel) in the mud design and (2) to select the concentration and particle size of mandarin peel powder whose application will improve the rheological and filtration properties of the mud, reduce the swelling of the clay rocks and increase the wellbore stability. These objectives were based on three main hypothesis: (i) adding of mandarin peel powder to a water-based mud will improve its filtration and rheological properties, (ii) mandarin peel powder will reduce the swelling of the clay rocks and improve the wellbore stability and (iii) toxicity of mud will be reduced with added mandarin peel powder into its composition.

1.6. Scientific contribution

The result of this research is defining the concentration and particle size of mandarin peel powder that can optimize the mud properties and increase the wellbore stability in different borehole conditions. Also, research shows mechanical and physicochemical mechanism by which mandarin peel powder particles act on mud properties and increase the wellbore stability and according to all obtained results confirms the applicability of the circular economy concept in the field of hydrocarbon exploration.

2. ORIGINAL SCIENTIFIC PAPERS

Paper 1: Medved, I., Gaurina-Međimurec, N., Novak Mavar, K. & Mijić, P. (2022a) Waste mandarin peel as an eco-friendly water-based drilling fluid additive. Energies, 15(7), 2591.

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Article

Waste Mandarin Peel as an Eco-Friendly Water-Based Drilling Fluid Additive

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Abstract: Drilling fluid represents the most important fluid that must fulfill numerous important assignments during drilling operations. Many commercially available additives for water-based drilling fluid fall into the category of non-degradable and environmentally hazardous materials. Significant development in this area can be made by using biodegradable materials as additives in drilling fluids. The objective of this study was to determine whether mandarin peel powder particle size affects the properties of the drilling fluid. In this paper, mandarin peel was used in the form of a dry powder divided into particle sizes smaller than 0.1 mm, and between 0.1 mm and 0.16 mm. Mandarin peel powder was added to a water-based drilling fluid in four different concentrations (0.5, 1, 1.5, and 2% by volume of water). By increasing the mandarin peel powder concentration, the API filtration reduced up to 42%, PPT filtration significantly decreased up to 61.54%, while the rheological parameters generally increased but remained within acceptable limits. It is determined that the optimal concentration of mandarin peel powder is up to 1.5% by volume of water.

Keywords: circular economy; mandarin peel powder; environmentally friendly additive; drilling fluid; API filtration; PPT filtration; rheological properties

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1. Introduction

During drilling operations, adequate design of the drilling fluid is a very important component. It must fulfill various tasks, such as transporting drill cuttings to the surface, controlling formation pressure, providing lubrication for the drill string, stabilizing the wellbore wall, and many others [1–6]. Drilling fluid is a complex fluid, thus its composition and properties affect the final drilling efficiency. For a successful drilling process, drilling fluid that will meet the conditions specific to each well should be selected [7]. Depending on the liquid phase, which is the basis for the preparation of this type of fluid, drilling fluid is divided into water-based, oil-based, synthetic, and special drilling fluids. Generally, oil-based drilling fluids are usually preferred for HTHP and ultra-HTHP drilling applications. Oil-based drilling fluid provides a high rate of penetration, a reduction in downhole fluid losses, shale stability, and reduced torque and drag [8–11]. However, the use of oil-based drilling fluid has been restricted by strict environmental protection laws due to the high toxicity of oil-based drilling fluid, and its high cost [12].

The problem of environmental protection has resulted in an increase in the use of water-based drilling fluid. Water-based drilling fluid consists mainly of fresh or salt water (>90%), active colloidal particles, inert particles, and chemical additives. Bentonite is an essential component of drilling fluid in water-based systems. It is widely used for its viscosity and filtration control. However, the density of a bentonite suspension is usually not sufficient to control the formation pressure, which means that the desired drilling fluid density must be achieved by the use of weighting agents. Weighting agents, such as barite, hematite, galena, or calcium carbonate, are chemically inert solid particles. Besides bentonite and barite, many other additives are used to control drilling fluid properties. Their classification based on specific functions is shown in Table 1.

Table 1. Drilling fluid additives with specific functions (Adapted from data in [13]).

Type of Additive	Action	Substances (Compounds)
Alkalinity/acidity control additives	Adjusting the pH value.	Lime, sodium hydroxide (caustic soda), sodium carbonate (soda ash), sodium bicarbonate.
Bactericide (biocide)	Killing bacteria in water-based drilling fluid containing natural starches and gums prone to bacterial degradation.	Aldehides, phenols.
Calcium reducers	Reducing Ca^{2+}.	Sodium hydroxide (caustic soda), sodium carbonate (soda ash), sodium bicarbonate, polyphosphates.
Corrosion inhibitors	Protecting equipment from corrosion.	Amine or organophosphate products, oxygen scavengers.
Deflocculants (thinners)	Reducing viscosity, preventing flocculation.	Low-molecular-weight anionic polymers. Tannins, polyphosphates, lignite, lignosulfonate.
Defoamers	Removing entrapped air and gas from drilling fluid systems.	Alcohol based defoamers, brine-based defoamer, acid fat based defoamers, silicone emulsion based defoamers.
Emulsifiers	Forming emulsion of two insoluble liquids.	Detergents, soaps, organic acids.
Filtration reducers	Reducing infiltration of the liquid phase of the drilling fluid through the filter cake into the formation.	Bentonite clays, lignite, CMC, polyacrylate, pregelatinized starch.
Flocculants	Causing flocculation of colloidal particles.	Salt hydrated lime, gypsum, sodium carbonate (soda ash), soda bicarbonate, sodium tetraphosphate, acrylamide-based polymers.
Foaming agents	Acting as surface active agents to foam into water.	Nonionic surfactants, contain polymeric materials.
Lost circulation materials	Bridging for fluid lost control.	Fiber, flake, granular/chemical thickening agents.
Lubricants	Reducing fluids coefficient of friction to minimize torque and drag.	Oils, synthetic liquids, graphite, surfactants, glycols, glycerine.
Shale inhibitors	Reducing shale hydration.	Soluble calcium or potassium, inorganic salts, organic compounds.
Surfactants	Surface tension decreasing, changing the colloidal state of clay.	Emulsifiers, demulsifiers, wetting agents, flocculants, deflocculants
Viscosifiers	Increasing viscosity, improving the hole-cleaning and solids-suspension ability.	Clay-based viscosifiers (bentonite), polymer and biopolymer viscosifiers.
Weighting agents	Increasing density of drilling fluid.	Barite, hematite, galena, calcium carbonate.

Focus on economics and performance in drilling activities and marginalization of environmental care has resulted in the use of toxic chemical additives in conventional water-based systems. These additives include sodium hydroxide, potassium chloride, potassium sulphate, polyamine, chromium-containing thinners, many shale stabilizers, and fluid loss additives, etc. [14–16]. Many commercially available additives for water-based drilling fluid fall into the category of non-degradable and environmentally hazardous materials [17]. There is a need to find and create new environmentally friendly additives that will contribute to the control of the drilling fluid properties in the same way, but with minimal impact on the environment [18,19]. Therefore, many studies have been and are still being conducted on using food waste [20] and other biodegradable materials as additives.

According to the World Bank, the world annually generates 2.01 billion tonnes of municipal solid waste (0.74 kg per person per day), of which 44% are food and green waste. By 2050 it is expected to grow up to 3.40 billion tonnes annually [21], which encouraged people to think about potential uses of food waste in order to reduce its amount, and at the same time obtain usable products. This requires a necessary change of a linear product lifecycle model, which has been applied thus far to an economy of reusing, remanufacturing, and recycling. In line with that, The European Green Deal, a new agenda for sustainable growth, requires global transition to a carbon-neutral, resource-efficient, and circular economy; this would reduce pressure on natural resources and energy consumption, while at the same time enable sustainable growth and new job creation. As one of its main strategy pillars, in 2020, the European Commission adopted the New Circular Economy Action Plan (CEAP). The plan oversees the entire life cycle of products, including their design, sustainable consumption, and waste prevention, bearing in mind that ways which imitate nature, where everything has value, are recognized as the only possible ways to reach a balance between progress and sustainability [22–24]. At the same time, the competitiveness of the oil industry in the world, where environmental protection has become a priority, depends on their adaptation possibilities. Oil companies are more concerned with their public images than ever before, and therefore are faced with inventing sustainable and environmentally friendly solutions which can ensure their survival. Significant development in this regard can be made with additives that are used in drilling fluid, for certain properties.

In the last few years, researchers have begun to undertake laboratory testing to determine whether food waste materials can be used as additives in water-based drilling fluids, in order to optimize the composition and properties of drilling fluids. As shown in Table 1, there are many additives on the market used to adjust different drilling fluid properties. However, most of the research relates to the possibility of using waste materials as additives to adjust the rheological and filtration properties. Table 2 shows eco-friendly water-based drilling fluid additives used thus far in tests, with their indicated influence on rheological parameters (plastic viscosity (PV), yield point (YP)), gel strength, API filtration, and drilling fluid cake thickness.

Rheological parameters are especially important since they affect cutting removal from the wellbore to the surface, resistance to drilling flow, and an increase in wellbore pressure, keeping cuttings and weighting additives in suspension during the period of circulation interruption, in addition to cutting release on the surface [25]. Plastic viscosity (PV) is a function of friction between solid particles in a drilling fluid, the amount of charge on these particles, and the viscosity of the dispersed phase. Yield point (YP) is a function of force between solid particles in the drilling fluid, and represents the capability of a drilling fluid to remove the cuttings from the annular space of the wellbore. Gel strength should be measured after 10 s and 10 min. Results obtained after 10 s (initial gel strength) show the minimum required shear stress to initiate fluid movement, and after 10 min indicate a measure of the thixotropic property of drilling fluid.

Filtration is the process of liquid phase separation from a drilling fluid into porous formation by the influence of differential pressure. Filtration rate and filtrate volume are directly related to the drilling rate, type of formation, formation damage, and differential sticking in the area of permeable rocks [26,27]. Generally, filtration can be defined as a measure of the drilling fluid's ability to cover a permeable formation with a thin and low-permeability cake.

In order to obtain a more pronounced effect of each additive on the properties of the drilling fluid, most of the tests are performed using a basic drilling fluid that contains only bentonite in addition to water. The waste materials are added in different concentrations (from 0.285% up to 16%), but in most cases small concentrations are added up to 4% by volume of water, as shown in Table 2.

Al-Hameedi et al. (2020) conducted laboratory testing with mandarin peel which was added to base drilling fluid that contained 600 mL water, 0.6 g NaOH, and 36 g of bentonite. Mandarin peel powder was added in four different concentrations: 1%, 2%, 3%, and 4% by volume of water. Rheological parameters, plastic viscosity (PV), and yield point (YP) were increased by adding mandarin peel powder. After adding 1% mandarin peel powder to a base drilling fluid, plastic viscosity increased from 7 mPa·s to 14 mPa·s, and continued to increase to 63 mPa·s with 4% of mandarin peel powder in the base drilling fluid. Yield point also increased from 5.61 Pa to 7.14 Pa with 1% of mandarin peel powder, and with 4% of mandarin peel powder in the base drilling fluid, the value of yield point was 29.07 Pa, which in practice results in excessive pressure loss. The results for 10-s gel strength showed a slight decrease by adding 1% and 2% of mandarin peel powder to the base drilling fluid, and an increase after adding 3% and 4%, with a maximum value of 12.24 Pa. The same trend was shown with results for 10-min gel strength, and the value was 14.18 Pa with 4% of mandarin peel powder in the base drilling fluid. API filtration with 1% mandarin peel powder significantly decreased from 12.5 mL to 7 mL, and by increasing the concentration to 4%, it continued to slightly decrease to 4 mL [28].

In 2020, mandarin production in Croatia was 38,172 tonnes [29]. In this study, from 1 kg of mandarin fruit, 72 g of mandarin peel powder was obtained, which leads to the conclusion that approximately 2750 tonnes of mandarin peel powder can be generated in Croatia every year. According to Al-Hameedi et al. (2020), the maximum concentration of mandarin peel powder was 4% by volume of water [28], but in this paper the highest tested concentration of mandarin peel powder was 2%; by increasing the concentration above 2%, considerable drilling fluid gelation occurred, and it was impossible to mix it. If it is considered that the required concentration of mandarin powder is 2%, based on the annual mandarin production in Croatia, about 137,500 m^3 of drilling fluid can be prepared. Mandarin peel waste generated annually in Croatia can be transformed into powder and used as a drilling fluid additive for more than 150 wells, which is much more than the domestic requirements.

Also, it is important to note that drilling operations generate a significant volume of drilling fluid waste that has to be properly treated and disposed of during and after drilling operations. Used drilling fluid represents the second largest volume of waste generated by the exploration and production part of the oil and gas industry [30,31]. Along with environmental protection, there is also significant cost for the disposal of environmentally hazardous waste. At some locations, there are other options for managing these types of waste, such as injection in deep underground formations [31–34]; waste optimization and reduction in waste volume to a minimum should be priorities [35].

In this paper, mandarin peel powder was used to determine its influence on rheological and filtration properties of bentonite-based drilling fluid. This type of food waste was chosen since mandarin is in second place in terms of fruit production in Croatia [29], and since other authors have found some useful properties of mandarin peel powder as an additive in drilling fluid [28,36,37].

The objective of the study was to determine whether mandarin peel powder particle size affects the properties of the drilling fluid. Compared to the research conducted by Al Hameedi et al. (2019 and 2020), the novelty of this research is manifested in a new detailed procedure of mandarin peel powder preparation (drying, grinding, sieving), as well as in the determination of the influence mandarin peel powder particle size (smaller than 0.1 mm, and between 0.1 and 0.16 mm) has on rheological and filtration properties (API filtration tests and PPT filtration tests (high pressure and high temperature conditions)).

Table 2. Eco-friendly water-based drilling fluid additives and their impact on drilling fluid properties.

Literature	Waste Material	Concentration, % by volume of Water	Tested Drilling Fluid Formulation	Rheology		Gel Strength	API Filtration	Cake Thickness
				Plastic Viscosity (PV)	Yield Point (YP)			
Al-Hameedi et al., 2019 and 2020 [16,28,36,37]	potato peel	1, 2, 3, 4	600 mL water, 0.6 g NaOH, 36 g bentonite	increase	decrease	decrease	decrease	decrease
	mandarin peel			increase	increase	up to 2% decrease, then increase	decrease	decrease
	fibrous food	1, 2	1000 mL water, 0.6 g NaOH, 60 g bentonite	increase	increase	increase	decrease	decrease
	palm tree leaves	1.5, 3	600 mL water, 1 g NaOH, 45 g bentonite	increase	decrease	decrease	decrease	decrease
	grass	0.5, 1, 1.5	spud drilling fluid	increase	increase	increase	decrease	decrease
	green olive pits	0.75 and 1.5	600 mL water, 0.6 g NaOH, 36 g bentonite	increase	increase	increase up to 0.75%, then decrease	decrease up to 0.75%, then increase	increase
Ghaderi et al., 2020 [3]	saffron purple petals	1, 2, 3	500 mL water, 0.03 wt% soda ash, 0.05 wt% NaOH, 3.5 wt% NaCl, 10 wt% bentonite	increase	increase	N/A	decrease	decrease
Al-Saba et al., 2018 [38]	banana peel	0.285, 0.57, 1.425	325.5 mL water, 24.5 g bentonite	significantly increase up to 0.285%, then significantly decrease	significantly increase up to 0.285%, then significantly decrease	significantly increase up to 0.285%, then significantly decrease	decrease	decrease
	olive pulp	0.57		increase	increase	increase	decrease	increase
	corncob	0.57, 1.71, 2.85		increase	increase	increase	decrease	decrease
	corn starch	0.57		decrease	increase	increase	decrease	decrease
	pomegranate peel	0.57		decrease	decrease	decrease	decrease	decrease
	tamarind gum	1.425, 2.85		N/A	N/A	N/A	decrease	decrease
	peach pulp	1.425		decrease	increase	increase	decrease	decrease
	coconut coir	1.425		N/A	N/A	N/A	increase	decrease
	soya bean peel	1.425		N/A	increase	increase	decrease	decrease
	sugar cane	1.425		increase significantly	increase	increase	decrease	decrease
	grass	1.425		increase	decrease	increase	increase	decrease
	henna	1.71, 2.85		increase	increase	increase	decrease	decrease
	coconut shell	1.71, 2.85		increase	increase	increase	decrease	decrease
Zhang et al., 2020 [39]	pomelo peel	1	600 mL water, 18.6 g bentonite	decrease	decrease	N/A	decrease	N/A

Table 2. *Cont.*

Literature	Waste Material	Concentration, % by volume of Water	Tested Drilling Fluid Formulation	Rheology		Gel Strength	API Filtration	Cake Thickness
				Plastic Viscosity (PV)	Yield Point (YP)			
Al-Hameedi et al., 2020 [40]	egg shell	0.75, 1.5	700 mL water, 0.2 g NaOH, 42 g bentonite	increase	increase	increase	decrease	decrease
Onolemhemhen et al., 2019 [41]	egg and snail shell	1.43, 2.86, 4.29, 5.71, 7.14, 8.57	350 mL water, 25 g bentonite, 90 g barite	N/A	N/A	N/A	N/A	N/A
Yalman et al., 2021 [42]	rice husk ash	2.1, 4.3, 7.5, 9.6, 13.4, 16	350 mL water, 22.5 g bentonite, 0.5 g xanthan gum (XG), 1 g carboxymethyl cellulose (CMC)	decrease	increase	increase	decrease up to 9.6%, then increase	increase

2. Laboratory Testing

The impact of adding mandarin peel powder to a bentonite-based drilling fluid on rheology and filtration properties was performed at the Drilling Fluid Laboratory (Department of Petroleum and Gas Engineering and Energy, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb) in Zagreb, Croatia.

2.1. Preparation of the Mandarin Peel Powder

This paper presents the use of mandarin peel powder as an additive used to optimize drilling fluid properties without environmental problems. The entire process of preparing mandarin powder from waste collection, to drying and grinding, is shown in Figure 1.

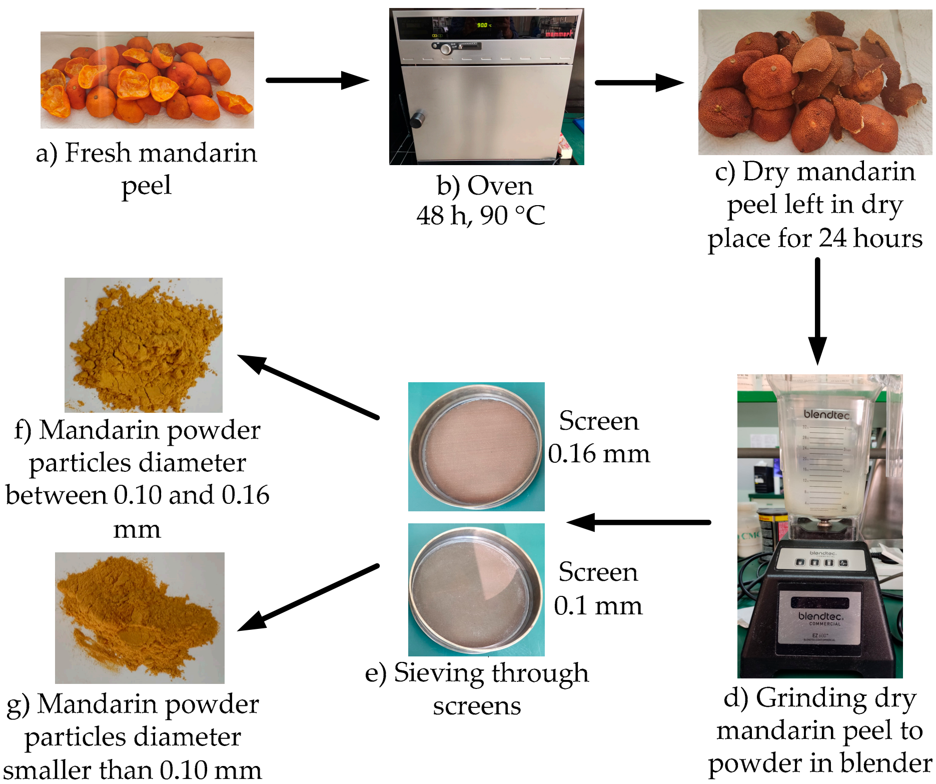


Figure 1. The entire process of preparing waste mandarin peel powder from waste collection.

After the waste mandarin peel was collected (a), it was first placed in an oven for 48 h at a temperature of 90 °C (b) in order to remove moisture from the peel. After 48 h of drying, the peel was left in a dry place for 24 h (c) and then ground and turned into powder using a blender (d). The resulting powder was sieved through two screens, first through one which had a 0.16-mm opening on the sieve (e). The particles that passed through this screen went to the next stage of sieving through a screen which had a 0.10-mm opening on the sieve (e). Thus, mandarin peel powder was divided into two groups of particle sizes, from 0.10 mm to 0.16 mm (f), and particles smaller than 0.10 mm (g). Mandarin peel powder of different particle sizes was used to check whether there were any differences in their useful properties for basic drilling fluid.

2.2. Drilling Fluids Composition

In order to examine the impact of the addition of mandarin peel powder on the rheological and filtration properties of bentonite-based drilling fluids, nine types of drilling fluids were prepared and subjected to laboratory testing: bentonite-based drilling fluid as a base drilling fluid (BDF), four drilling fluids containing mandarin peel powder with particles smaller than 0.1 mm (labelled with A), and four drilling fluids containing mandarin peel powder with particles between 0.1 and 0.16 mm (labelled with B), as shown in Table 3. The mandarin peel powder was added in four different concentrations: 0.5, 1, 1.5, and 2% by volume of water, in order to determine the influence of concentration and particle size on drilling fluid properties. Drilling fluids with 4% mandarin powder were also prepared, but they gelled very quickly, and it was impossible to mix them further; hence, the maximum selected concentration was 2% by volume of water. Drilling fluids were prepared according to American Petroleum Institute Standards, API Specifications 13A and API 13B-1 [43].

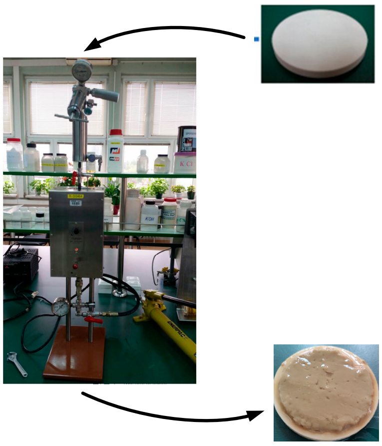
Table 3. Composition of drilling fluids used in this study.

Composition	BDF	A1	A2	A3	A4	B1	B2	B3	B4
Water (mL)	1000	1000	1000	1000	1000	1000	1000	1000	1000
Bentonite (g)	60	60	60	60	60	60	60	60	60
NaOH (g)	1	1	1	1	1	1	1	1	1
Mandarin peel powder (% by volume of water)	-	0.5	1	1.5	2	0.5	1	1.5	2

2.3. Laboratory Test Equipment and Conditions

After preparation of the drilling fluids, filtration and rheological properties, in addition to gel strength, were measured for all nine drilling fluids. The equipment and conditions used are shown in Table 4.

Table 4. Laboratory test equipment and conditions.

Test	API Filtration	PPT Filtration	Rheology and Gel Strength
Equipment	 API Filter Press (Baroid, Houston, TX, USA)	 Permeability Plugging Tester (OFI Testing Equipment, Houston, TX, USA)	 Fann Viscometer 35 A (Fann Instruments, Houston, TX, USA)
Conditions	Pressure of 6.895 bar (100 psi) and room temperature	Differential pressure of 34.47 bar and temperature of 88 °C	Atmospheric pressure and room temperature

3. Results

3.1. API and PPT Filtration

Filter paper Whatman No. 50 with a filtration area of 45.8 cm^2 (7.1 in^2) was placed in the bottom of the API filter press cell. After preparation of drilling mud, it was poured into a cell. A pressure of 6.895 bar (100 psi) was applied to the drilling fluid for a period of 30 min. The volume of filtrate extracted from the drilling fluid through the filter paper was gathered in a measuring cylinder, while a drilling fluid cake was formed on the filter paper. Filtrate volume measured after 30 min represents API filtration.

Based on the results of API filtration, by increasing the mandarin powder concentration the API filtration reduces, as shown in Table 5. The lowest API filtration was measured with B4 drilling fluid (10 mL), relative to a value measured with BDF (18 mL). The drilling fluid cake thicknesses were slightly reduced by the addition of mandarin peel powder compared to the drilling fluid cake thickness measured with BDF (1.5 mm).

A device used for determining the ability of the drilling fluid to plug pores in a ceramic disc is called a Permeability Plugging Tester (PPT), which represents a modification of the standard HTHP filter press. After preparation of drilling mud, it was poured into a PPT cell. The required pressure is applied with a pump on the lower side, which pushes the mud through a ceramic disk placed on the upper side of the cell. The filtrate was collected in a receiver after 7.5 and 30 min. The filtration area is 22.9 cm^2 (3.5 in^2), twice as low as that of API filtration, and the filter medium is a ceramic disc. The permeability of used ceramic discs was 0.75 μm^2 (750 mD), and the tests were carried out at a differential pressure of 34.47 bar and a temperature of 88 °C. Since the filtration surface in API filtration is twice as large, fluid volume collected after 30 min needs to be multiplied by 2 (Equation (1)), while the initial filtration or spurt loss can be calculated using Equation (2) [44]:

$$\text{PPT filtrate volume} = 2 \cdot V_{30} \quad (1)$$

$$\text{Spurt loss} = 4 \cdot V_{7.5} - 2 \cdot V_{30} \quad (2)$$

where:

PPT filtrate volume, mL;
$V_{7.5}$—fluid volume collected after 7.5 min, mL;
V_{30}—fluid volume collected after 30 min, mL;

Spurt loss—fluid volume collected before forming a drilling fluid cake, mL.

The PPT filtration test was performed only with those drilling fluids where the greatest reduction in API filtration was measured for both tested mandarin peel particle sizes, which were the A4 and B4 drilling fluids. Table 6 shows the results of PPT filtration through a ceramic disc with a permeability of 0.75 μm^2 (750 mD).

Table 5. API filtration.

Time (min)	**BDF**	**A1**	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**
	API Filtration (mL)								
2.5	5.5	4.5	4	3	3.5	4.5	4	3	2.5
5	7.5	5.5	5.5	4.5	4.5	6.5	5.5	4.5	3.5
7.5	9.5	7	6.5	5.5	5.5	7.5	6.5	5	4.5
10	10.5	8	8	6.5	6.5	9	7.5	6	5.5
12.5	12	9	9	7.5	7.5	10.5	8.5	6.5	6.5
15	13	10	9.5	8	8	11.5	9	7.5	7
17.5	14	10.5	10.5	8.5	9	12	10	8	7.5
20	15	11	11	9	9.5	13	10.5	8.5	8
22.5	16	12	12	10	10	14	11	9	8.5
25	17	12.5	12.5	10.5	10.5	14.5	11.5	9.5	9
27.5	17.5	13	13	11	11	15	12	10	9.5
30	**18**	**13.5**	**13.5**	**11.5**	**11.5**	**16**	**13**	**10.5**	**10**

Table 6. PPT filtration through a ceramic disc with a permeability of 0.75 μm^2 (750 mD).

	Disc Permeability—0.75 μm^2 (750 mD) Differential Pressure—34.47 bar		
	Temperature—88 °C		
Drilling fluid	BDF	A4	B4
Concentration of mandarin peel powder, % by volume of water	0	2	2
$V_{7.5}$, mL	17	8	6
V_{30}, mL	26	11	10
PPT filtrate volume, mL	52	22	20
Spurt loss, mL	16	10	4

Filtration through the ceramic disc, which has a permeability of 0.75 μm^2 (750 mD), showed a significant decrease in filtration volume after 30 min for both tested drilling fluids containing mandarin peel powder in a concentration of 2% by volume of water (A4 and B4) (20 and 22 mL), relative to values measured with BDF (52 mL). Observing the spurt loss values, the amount of fluid that was lost before forming the drilling fluid cake was significantly decreased for both tested drilling fluids containing mandarin peel powder in a concentration of 2% by volume of water (A4 and B4) (4 and 10 mL), relative to values measured with BDF (16 mL). Since the tested disk has pores of different sizes, it is assumed that mandarin peel particles (particles between 0.1 and 0.16 mm) better plugged the disc pores relative to particles smaller than 0.1 mm where a certain amount of these particles passed through the disc before forming the drilling fluid cake.

3.2. Rheology of Tested Drilling Fluids

The rheological properties of all tested drilling fluids were determined using a Fann viscometer 35A. Shear stresses were obtained at six fixed speeds of 600, 300, 200, 100, 6, and 3 rpm. The plastic viscosity (PV) of all the tested drilling fluids was calculated according to Equation (3), and the yield point (YP) was calculated according to Equation (4) [45]:

$$PV = \theta_{600} - \theta_{300} \quad (3)$$

$$YP = 2 \cdot \theta_{300} - \theta_{600} \quad (4)$$

where, θ_{600} and θ_{300} are the 600 and 300 RPM dial readings, respectively.

The results of plastic viscosity (PV) and yield point (YP) are shown in Figure 2, YP/PV ratio in Figure 3, while results of 10-s gel and 10-min gel strengths for all tested drilling fluids are shown in Figure 4.

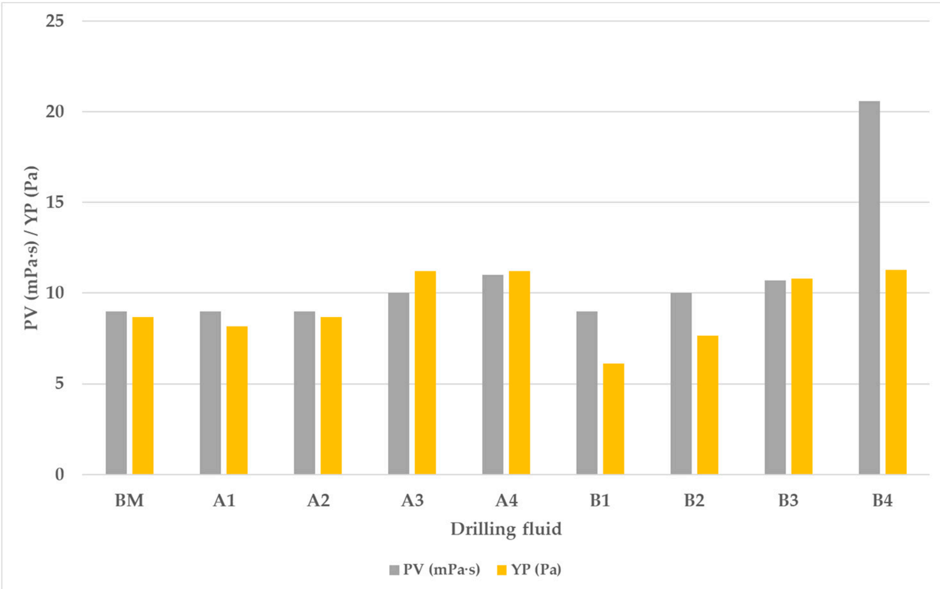


Figure 2. Plastic viscosity (PV) and yield point (YP) of all tested drilling fluids.

It was determined that increasing the concentration of mandarin peel powder generally increases all the values of rheological parameters (PV and YP) and the 10-s gel and 10-min gel strengths. The highest values of rheological parameters (PV and YP) were measured with A4 and B4 drilling fluids (11 mPa·s and 11.22 Pa, and 21 mPa·s and 11.27 Pa, respectively), relative to values measured with BDF (9 mPa·s and 8.67 Pa, respectively). By increasing the YP/PV ratio, the cutting carrying capacity of the drilling fluid increased [46]. It is shown that by addition of mandarin peel powder in a concentration of 1.5% by volume of water and higher, the cutting carrying capacity increases. The exception is B4 mud, since it has a high PV value and therefore a smaller value of YP/PV. Moreover, the highest values of 10-s gel and 10-min gel strengths were measured with A4 and B4 drilling fluids (10.71 Pa and 18.36 Pa, and 12.75 Pa and 22.95 Pa, respectively), relative to values measured with BDF (6.12 Pa and 15.81 Pa, respectively).

In order to explain in more detail, the influence of concentration of mandarin peel powder on the rheological properties of the drilling fluid, the pressure loss values in annular (per 1 m of pipe length) were determined for all tested drilling fluids, which can be seen in Table 7. The pressure loss around the drill pipes and drill collars was calculated for the case when wellbore was drilled with a bit having a diameter of 0.2159 m (8 1/2 in). Drill collars had an outside diameter of 0.17145 m (6 3/4 in), and drill pipes had an outside diameter 0.127 m (5 in). The drilling fluid pump flow rate was 1600 L/min.

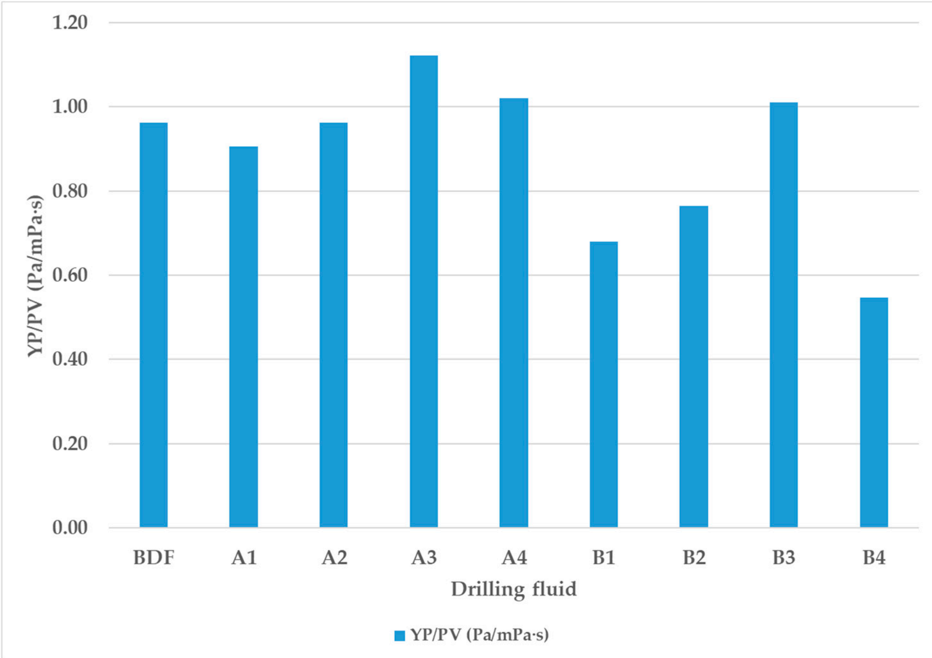


Figure 3. YP/PV ratio of all tested drilling fluids.

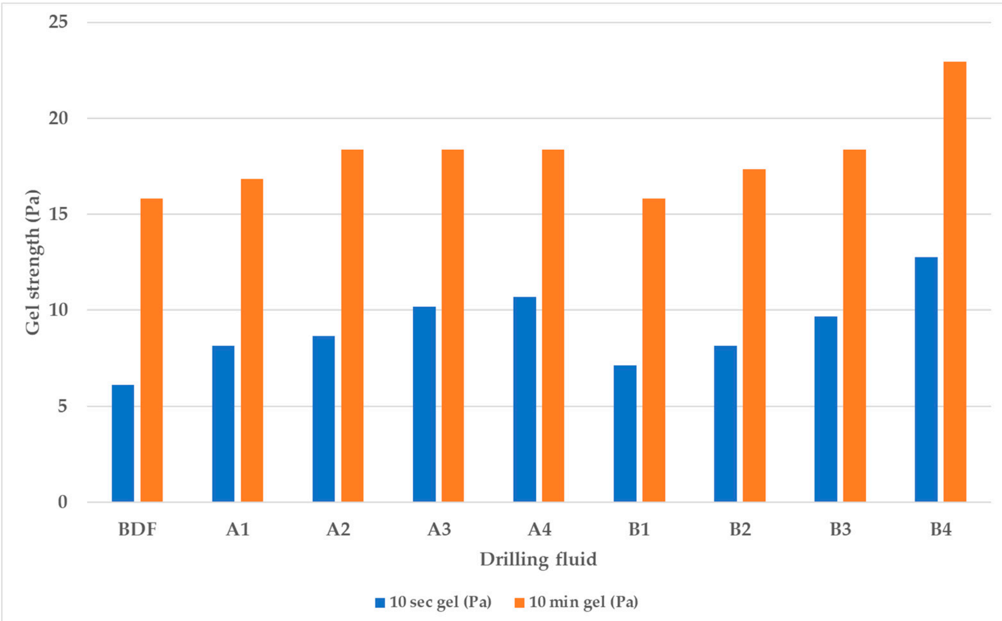


Figure 4. The 10-s gel and 10-min gel strengths of all tested drilling fluids.

Table 7. Pressure loss per 1 m of pipe length.

Drilling Fluid Flow	BM	A1	A2	A3	A4	B1	B2	B3	B4
	Pressure Loss (Pa/m)								
Around drill pipe	451	428	451	572	579	336	411	458	567
Around drill collar	1821	1821	1807	1846	1866	1821	1846	1846	2012

The density of the basic drilling fluid (BDF) was 1030 kg/m^3, while the addition of mandarin powder slightly reduced its value up to 1010 kg/m^3, at a maximum tested concentration of mandarin peel powder of 2% by volume of water. The main reason for the decrease in the density of the drilling fluid is the entry of air into drilling fluid during the mixing. Al-Hameedi et al. (2020) noticed the same phenomenon [28].

With the stated geometry of the wellbore, geometry of used drilling tools, and the flow conditions, the flow around the drill pipes was laminar, and around the drill collars turbulent, as shown in Figure 5.

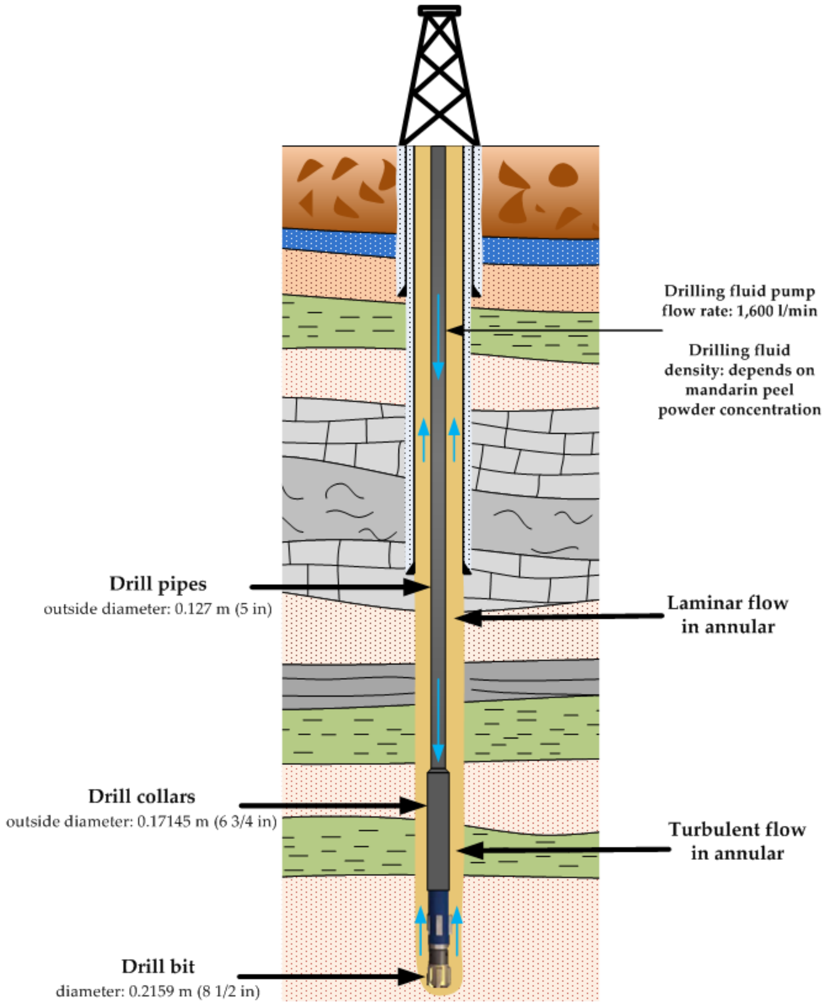


Figure 5. Input data for the calculation of the pressure loss in the annular.

For laminar flow the pressure loss is calculated according to Equation (5), while for turbulent flow is calculated according to Equation (6) [47]:

$$p = \frac{48 \cdot l \cdot \mu_e \cdot v}{(D_2 - D_1)^2} \quad (5)$$

$$p = \frac{0.1275 \cdot l \cdot \rho_i^{0.8} \cdot v^{1.8} \cdot {\mu_e}^{0.2}}{(D_2 - D_1)^{1.2}} \quad (6)$$

where:

v—flow rate of the drilling fluid in the annular space (m/s);
ρ_i—drilling fluid density (kg/m^3);
μ_e—effective viscosity (Pa·s);
D_2—drill bit diameter or inside diameter of casing (m);
D_1—outside diameter of drill pipe/collar (m);
l—pipe length (m).

For a turbulent type of flow, the effective viscosity value is the same as PV, while for laminar flow, it is calculated according to Equation (7) [47]:

$$\mu_e = PV + \frac{YP}{\frac{12 \cdot v}{D_2 - D_1}} \tag{7}$$

where:

v—flow rate of the drilling fluid in the annular space (m/s);
PV—plastic viscosity (Pa·s);
YP—yield point (Pa);
D_2—drill bit diameter or inside diameter of casing (m);
D_1—outside diameter of drill pipe/collar (m).

As expected, it is shown that generally pressure loss increases by increasing the concentration of mandarin peel powder for flow around the drill collar. For laminar flow, an increase in pressure loss was observed at higher concentrations than 1.5% of mandarin powder while at lower concentrations (below 1% of mandarin peel powder) it is even less than the pressure loss calculated with basic drilling fluid (BDF).

4. Discussion

To determine the influence of the concentration and particle size of mandarin peel powder, a comparison of all results was made. Table 8 shows a reduction in API filtration for all tested drilling fluids relative to API filtration of base drilling fluid (BDF), expressed as percentages.

Table 8. Reduction in API filtration for all tested drilling fluids.

Drilling Fluid Sample	Reduction in API Filtration (%)
A1	25
A2	25
A3	36
A4	36
B1	11
B2	28
B3	42
B4	44

It is shown that the highest reduction in filtrate volume was obtained with drilling fluids which contain large amounts of mandarin peel powder (2%), drilling fluids A4 and B4; meanwhile, the highest value was obtained with B4 drilling fluid (44%) which contains larger particles (between 0.1 and 0.16 mm). Comparing results obtained at the concentrations of 1, 1.5, and 2% of mandarin powder, better results were obtained with powder having larger particles (between 0.1 and 0.16 mm) (28%, 42%, and 44%, versus 25%, 36%, and 36%, respectively).

Table 9 shows a reduction in PPT filtration and spurt loss for A4 and B4 drilling fluids relative to values measured with base drilling fluid (BDF), expressed as percentages.

Table 9. Reduction in PPT filtration and spurt loss for all tested drilling fluids.

Drilling Fluid	Reduction in PPT Filtration (%)	Reduction in Spurt Loss Volume (%)
A4	57.69	37.5
B4	61.54	75

It is shown that PPT filtration and spurt loss significantly decreased for both tested drilling fluids (A4 and B4), compared to values measured with a base drilling fluid (BDF). Comparing both results, better results were obtained with powders containing larger particles (between 0.1 and 0.16 mm). Although a slight decrease in PPT filtration was observed (61.54% compared to 57.69%), the value of spurt loss was significantly reduced (75% compared to 37.5%).

Table 10 shows an increase/decrease in rheological parameters and gel strength values relative to values obtained with base drilling fluid (BDF), expressed as percentages.

Table 10. Increase/decrease values of rheological parameters.

Parameter	**Increase (+)/Decrease (−) (%)**							
	A1	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**
PV (mPa·s)	0	0	11	22	0	11	19	129
YP (Pa)	−6	0	29	29	−29	−12	25	30
YP/PV (Pa/mPa·s)	−6	0	16	6	−29	−21	5	−43
10 s gel (Pa)	33	42	67	75	17	33	58	108
10 min gel (Pa)	6	16	16	16	0	10	16	45

By increasing the concentration of mandarin peel powder, plastic viscosity increased slightly up to a concentration of 1.5%. For drilling fluids containing larger mandarin particles (between 0.1 and 0.16 mm), after increasing the mandarin peel powder concentration up to 2%, a significant increase in PV (129%) was obtained. Generally, particle size does not have much of an impact on PV, since up to a concentration of 1.5% similar values were obtained.

Yield point values at concentrations up to 1% are even smaller than those obtained with BDF, while at higher concentrations they follow the results of plastic viscosity such that increasing the concentration increases its values. When comparing the influence of particle size on YP values, it is shown that similar values were obtained at concentrations of 1.5 and 2% by volume of water.

YP/PV ratio has a similar trend as the YP value, with the exception of B4 mud where a significant increase in PV was obtained (129%). It can be seen that for improving the cutting carrying capacity, concentration of mandarin peel powder should be 1.5% by volume of water or higher, but even at lower concentrations, the decrease in value is not significant, especially in drilling fluids that contain mandarin peel powder particles smaller than 0.1 mm.

It is shown that increasing the concentration of mandarin peel powder significantly increases the 10-s gel strength (33% to 75% for drilling fluids with smaller particles than 0.1 mm, and 17% to 108% for drilling fluids with particles between 0.1 and 0.16 mm), while they slightly increase the 10-min gel strength except in the case when mandarin peel powder (particles between 0.1 and 0.16 mm) was added at a concentration of 2% (B4 drilling fluid), and the gel-strength increase amounted to 45%.

Table 11 shows an increase/decrease of pressure loss values relative to values obtained with base drilling fluid, expressed as percentages.

It is shown that a concentration of mandarin peel powder below 1% reduces pressure loss around the drill pipe and drill collar, which corresponds to the results of plastic viscosity and yield point. For laminar flow, by adding smaller particle sizes (up to 0.1 mm) higher pressure losses were calculated for concentrations of 1.5% (26.8%) and 2% (28.4%); meanwhile, for larger tested particles (between 0.1 and 0.16 mm), higher pressure losses were calculated for a concentration of 2% (25.7%). For turbulent flow, only the addition of 2% mandarin peel powder (particles between 0.1 and 0.16 mm) increased pressure loss by 10.5%, while in other cases the impact was negligible.

Table 11. Increase/decrease values of pressure loss values.

Pressure Loss	Increase (+)/Decrease (−) (%)							
	A1	A2	A3	A4	B1	B2	B3	B4
Around drill pipe	−5.1	0.0	26.8	28.4	−25.5	−8.9	1.6	25.7
Around drill collar	0.0	−0.8	1.4	2.5	0.0	1.4	1.4	10.5

Comparing the results with previous research, increases in the values of rheological parameters are somewhat more moderate compared to the results of Al-Hameedi et al. [28], who obtained significant increases of rheological parameters at a lower concentration of 1% (PV increase 100%, YP increase 27%), while gel strength values decreased up to 2% by volume of water, then increased, with the highest values measured at a concentration of 4% by volume of water. Moreover, the API filtration decreased significantly (44%), even at a low concentration of mandarin peel powder (1% by volume of water); meanwhile, in this study a concentration of 4% by volume of water was required to obtain a similar decrease in API filtration. Additionally, it was found that a lower concentration of mandarin peel powder, up to 1.5% by volume of water, is needed to achieve optimal properties.

In general, based on the research results, it can be concluded that by increasing the concentration of mandarin peel powder, rheological parameters increase and filtration decreases. According to Ojha et al. (2016), the solubility of mandarin powder in water is about 28% [48]; thus it can be assumed that the viscosity of the filtrate increases, thereby increasing the resistance to leakage of the filtrate through a drilling fluid cake/ceramic disc, which consequently results in a decrease in filtration value. In addition, plugging of the pores of the drilling fluid cake is likely to occur, and in order to gain better insight, it is necessary to obtain SEM images of the drilling fluid cake to determine the possible mechanisms for the reduction in filtrate loss.

5. Conclusions

Based on laboratory testing, the following conclusions can be drawn:

- Mandarin peel powder particle size and concentration have influence on drilling fluid properties.
- By increasing the mandarin powder concentration, the API filtration decreases.
- PPT filtration significantly decreased by 61.54% and 57.69% with A4 and B4 drilling fluids, respectively.
- Spurt loss significantly decreased by 75% and 37.5% with A4 and B4, respectively.
- By adding mandarin peel powder (particles less than 0.1 mm), rheological parameters generally increase and remain within acceptable limits.
- By adding mandarin peel powder (particles between 0.1 and 0.16 mm), rheological parameters generally increase. At a concentration of 2%, PV and 10-s gel strength values significantly increase, resulting in increased pressure loss.
- Comparing the particle sizes of mandarin peel powder, it can be concluded that slightly better results were obtained with larger particles between 0.1 and 0.16 mm, but for field operations both sizes yield satisfactory drilling fluid properties.
- In general, it can be concluded that the optimal concentration of mandarin peel powder is up to 1.5% by volume of water.

These data provide a good basis for further testing with other food waste which can also be used as an additive to optimize drilling fluid properties. In addition, determining drilling fluid properties in more complex drilling fluid compositions is recommended.

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the introduction section and figures. All authors have read and agreed to the published version of the manuscript.

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Article

Green Approach in Water-Based Drilling Mud Design to Increase Wellbore Stability

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Abstract: Wellbore instability is one of the most serious problems that can occur during drilling, mainly during drilling oil or gas wells through rocks that contain a higher proportion of clay, such as shales. To prevent wellbore instability, oil companies apply different approaches to strengthen wellbore walls, and use different shale swelling inhibitors. The aim of this research was to apply a green approach and the concept of the circular economy in mud design, and to determine whether mandarin peel powder, which is a waste material, can be used as an inhibitor of shale swelling. For that purpose, pellets consisting of bentonite and quartz in a 50:50 ratio were prepared using a compactor, and bentonite-based drilling mud (BM) with and without mandarin peel powder in concentrations of 0.5, 1, 1.5 and 2% by volume of water. The swelling of quartz–bentonite pellets after 2 and 24 h in each drilling-mud sample was determined at room temperature and 90 °C using a linear swell meter. On the basis of laboratory research, we concluded that increasing the concentration of mandarin peel powder reduces pellet swelling. By adding mandarin peel powder particles between 0.1 and 0.16 mm to the base mud at a concentration of 2% by volume of water, the following was achieved: 44% reduction in API filtration, 61.54% reduction in PPT filtration, 45% reduction in pellet swelling after 24 h at room temperature, and 48.6% reduction of pellet swelling after 24 h at 90 °C.

Keywords: waste mandarin peel; wellbore instability; drilling mud; quartz–bentonite pellet; swelling; mud filtration

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1. Introduction

The successful construction of a wellbore is an extremely challenging technical and technological process, as each well presents its own specific challenges. Due to a number of potential problems, drilling can be significantly slowed down, and, in extreme cases, the well may be abandoned, resulting in significant financial losses. With the increasing depth of drilled wells and the increasing number of horizontal extended reach wells, the oil and gas industry faces many issues that were not as pronounced in vertical wells. According to the available data, solving problems related to wellbore instability annually costs the oil industry between USD 0.5 and 1 billion [1–3]. The most complex problems in the technology of deep well drilling arise from the disturbed stability of the wellbore walls due to the effect of various factors. Wellbore instability is defined as any undesirable change in the diameter (narrowing or widening) of the wellbore relative to the diameter of the drill bit used to drill a particular section of the wellbore, and is one of the major problems in drilling operations. The consequences of wellbore instability can vary, such as the difficult cleaning of the well, the demanding execution of cementing operations and logging measurements, problems with drill string tripping or casing run-off, which ultimately leads to an increase in the time planned for drilling, and the need to allocate additional resources to eliminate the negative consequences [3–7].

The causes of wellbore instability are numerous and vary depending on how they affect the stability of the wellbore. In most cases, wellbore instability is the result of several causes acting simultaneously. They are usually divided into two groups [5,8]: mechanical and physicochemical causes. Figure 1 illustrates different situations that can cause wellbore instability.

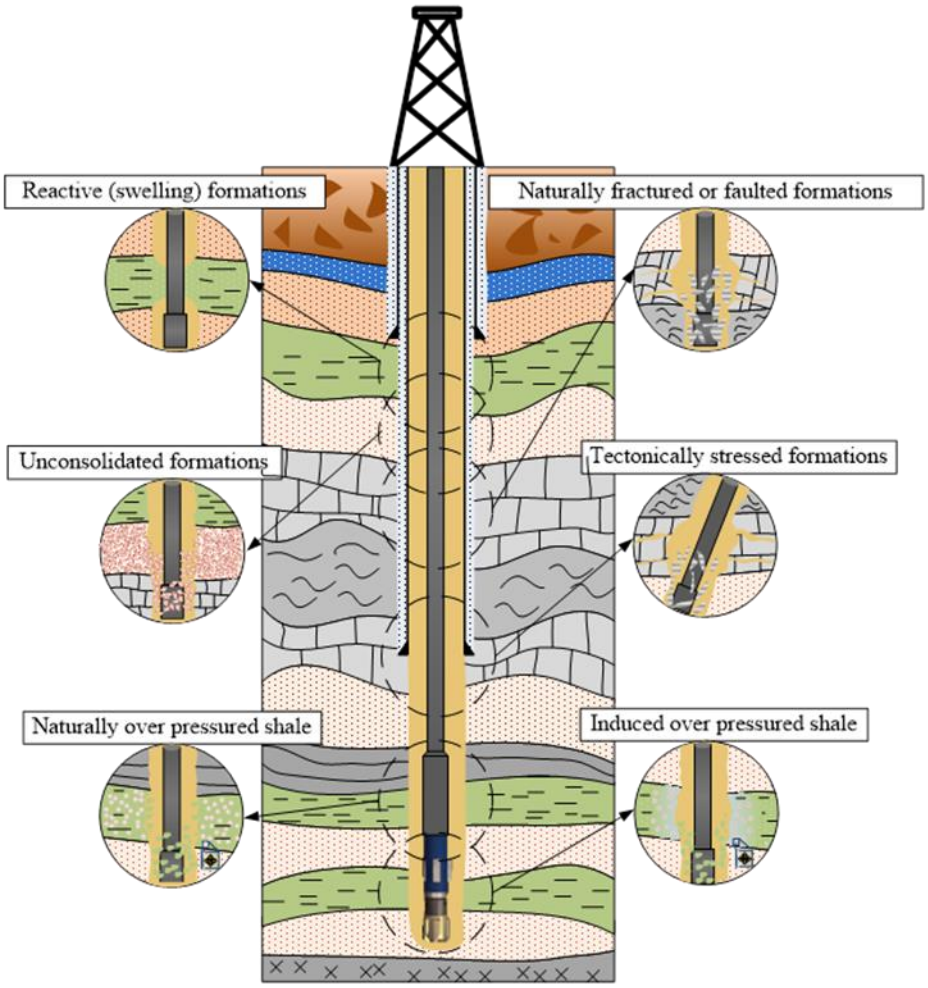

Figure 1. Examples of situations that can cause wellbore instability (according to [3]).

Mechanical causes of wellbore instability result from the mechanical properties of drilled subsurface formations and from changes in stresses on the wellbore walls, while physicochemical causes are due to the interaction between rock and drilling mud. This classification can only be considered to be a framework, while wellbore instability is usually in reality the result of both groups of causes [9–11].

To understand the mechanical causes of wellbore instability, it is necessary to compare the state of the rock immediately before and after the wellbore is drilled through. From a rock mechanics point of view, the rock is in a natural stress equilibrium before drilling. This equilibrium state of the rock at a given depth is primarily the result of overburden (lithostatic) pressure, but also of various additional stresses resulting from tectonic activity. The moment at which the drill bit penetrates a particular rock, the existing equilibrium state is disturbed, and a new stress system is created on the wellbore walls and in the zone close to the borehole. The new stress distribution is due to a certain drilled rock volume being replaced by a mud column with a certain density. Axial (σ_a), radial (σ_r), and tangential (σ_t) stresses occur at the wellbore walls, while the original local (in situ) stresses continue to act at a certain distance from the well [12]. The values and stress distributions on wellbore walls depend on the combined action of mechanical, chemical, thermal, and hydraulic effects [13]. Another form of instability that can occur during drilling is rock fracture or tensile failure, which occurs when the effective value of any of the three principal stresses exceeds the tensile strength of the rock. In addition, the angle connecting the axis of the wellbore to a particular subsurface formation layer plays an important role in the stability of the wellbore. According to Labensky et al. (2003), the probability of instability increases as the angle between the axis of the wellbore and the dip angle (undip or downdip) of the formation layer decreases, while the greatest stability is achieved when the formation layer is drilled through at an angle of 90°. When designing a well, the relationships between the individual components of the local (in situ) stresses and their orientation must be taken into account [4].

Simultaneously with the process of stress redistribution on the wellbore walls that occurs during drilling, physicochemical interactions between drilling mud and rock may also occur. Various mechanisms that destabilize the wellbore can occur if the composition of the mud is not properly defined. Wellbore instability caused by physicochemical causes is most commonly associated with shale rocks due to their high clay mineral content and extremely low permeability [14–16]. Shale is usually composed of the following minerals: quartz, calcite, and clay from the smectite group (mostly montmorillonite), illite, chlorite, and kaolinite in varying proportions [3,17,18]. In shale, which comprises a significant amount of clay in its composition, hydration can occur during the drilling of this formation, which is a significant obstacle to successful well construction. In addition, shale is composed of mixed clay minerals in varying proportions, and their hydration behavior is difficult to predict. The behavior of shale as a rock directly depends on the behavior of a particular type of clay mineral. Each of these clay minerals has a specific crystalline structure that also determines its reaction with the mud, especially in water-based mud with respect to the reactivity of water with the clay minerals [3]. This problem is even more significant, because this type of mud is the most commonly used for drilling [19–22], as it is more environmentally friendly and cheaper than oil-based muds. Due to the relatively low permeability of the shale, mud cake is not formed on the wellbore walls [23]. The direct consequence of the nonexistence of mud cake is the rapid movement of water molecules into the pore space of the shale and an increase in pore pressure in the near-wellbore zone over time. In addition to the increase in pore pressure due to unfavorable interactions between mud and shale rock, there may also be changes in the mechanical properties of the rock, such as strength and Young's modulus [24,25].

According to literature, 90% of all well stability problems occur when drilling through shales, formations that account for 75% of all formations through which a well is drilled [8,26–29]. The contact of shale with water from mud can cause shale hydration, changing the volume of the rock and reducing its cohesive strength. The excessive hydration of shales during drilling can lead to several problems. The main problem is the swelling of clay minerals, which creates a condition for the occurrence of wellbore instability. In addition to wellbore instability, there are other negative consequences of excessive hydration during drilling, such as excessive mud viscosity, stuck pipes, lower mechanical drilling speed, and bit balling [30–32]. However, it is very difficult to single out hydration as the cause of shale swelling and wellbore instability. In addition, several different processes occur during the contact between mud and rock, such as the aforementioned hydration (adsorption or absorption of water), ion diffusion flow (change in the interlayer space of the clay particles), mud filtrate flow due to overpressure in the wellbore, and capillary action [11]. A common feature of these processes is the movement of water and ion molecules into or out of the shale, and that they occur simultaneously. In some situations, different mechanisms can simultaneously cause water and ions to move in opposite directions. These processes continue until equilibrium is reached between rock and mud. Whether and to what extent such processes develop primarily depend on the mineralogical composition of the clay rock, but also on the properties of the mud in contact with the rock. In order to avoid the physicochemical causes of wellbore instability, the composition of the mud used when drilling through a particular rock must be precisely defined.

Although a certain composition of drilling mud gives satisfactory results in wellbore stabilization, recent research indicates that the problem has not yet been completely solved. The most commonly used additives to prevent clay hydration are various types of salts such as KCl, NaCl, NH_4Cl, or $CaCl_2$, and permanent inhibitors such as quaternary amine polymers [3]. When drilling through rocks that are prone to wellbore instabilities, mud composition can be optimized to have the lowest possible filtration value to minimize the amount of filtrate that penetrates the rocks of the near-wellbore zone, reacting with the clay components. However, a small amount of water always penetrates the rock before the mud cake forms, if it is created at all, as in the case of drilling through the shale formation. Therefore, it is necessary to minimize filtration by using additives such as starch, gum, and cellulose.

Since some commercially available water-based drilling mud additives fall into the category of environmentally hazardous substances (NaOH, KOH, K_2SO_4, polyamine, chromium-containing thinners, many shale stabilizers and mud loss additives, etc.), the new stricter environmental norms require the development of new ecofriendly additives for the adequate control of drilling mud properties with minimal environmental impact [33–35].

In the last decade, researchers have conducted laboratory tests to examine if waste materials can be added to water-based mud to optimize filtration properties. Table 1 lists food waste that has been used to optimize the filtration properties of water-based muds. Most of the tests were conducted with bentonite-based mud (bentonite suspension), which mainly consists of water, bentonite, and additives for pH adjustment, so Table 1 does not provide information on the composition of each mud type. Although the additives were added at different concentrations, most of the examined additives generally reduce API filtration by increasing the concentration, and Table 1 shows the highest measured value. Exceptions are green olive pits, which decrease API filtration up to a concentration of 0.75% of water volume and then increase it [36], and rice husk ash, which decreases API filtration up to a concentration of 9.6% and then increases it [37]. The range of filtration reduction for different waste materials is thus very wide, ranging from 9% to 68% for mandarin peel powder. To gain better insight into the potential of using these additives to optimize drilling mud, additional properties need to be tested. The effect of waste materials on rock swelling has not yet been studied in detail. Zhang et al. (2020) measured the swelling of a bentonite pellet in a pomelo powder solution. The pellets were compressed at 34.48 MPa (5000 psi) for 30 min. The concentration of the pomelo powder was 0.3, 0.5, 0.7, and 1% of the volume of water added to the base mud consisted of 600 mL of water and 18.6 g of bentonite. They concluded that, as the concentration of pomelo powder increased, the swelling of the pellet decreased to about 62, 60, 50, and 48% after 24 h compared to the swelling in distilled water (about 70%) [38].

Table 1. Waste materials used to optimize the filtration properties of water-based muds.

Literature	Waste Material	Concentration (%) by Volume of Water	Highest Measured Reduction in Filtration (%)
Al-Hameedi et al., 2019 and 2020 [35,36,39,40]	Potato peel	1, 2, 3, 4	30
	Mandarin peel		68
	Fibrous food	1, 2	30
	Palm tree leaves	1.5, 3	32
	Grass	0.5, 1, 1.5	48
	Green olive pits	0.75 and 1.5	16.7
Ghaderi et al., 2020 [41]	Saffron purple petals	1, 2, 3	45

Table 1. *Cont.*

Literature	Waste Material	Concentration (%) by Volume of Water	Highest Measured Reduction in Filtration (%)
Al-Saba et al., 2018 [42]	Banana peel	0.285, 0.57, 1.425	32
	Olive pulp	0.57	44
	Corncob	0.57, 1.71, 2.85	46.4
	Corn starch	0.57	20.8
	Pomegranate peel	0.57	20.0
	Tamarind gum	1.425, 2.85	64.0
	Peach pulp	1.425	44.0
	Soya bean peel	1.425	60.0
	Sugar cane	1.425	28.8
	Henna	1.71, 2.85	48.0
	Coconut shell	1.71, 2.85	52.0
Zhang et al., 2020 [38]	Pomelo peel	1	26.2
Al-Hameedi et al., 2020 [43]	Egg shell	0.75, 1.5	34.6
Yalman et al., 2021 [37]	Rice husk ash	2.1, 4.3, 7.5, 9.6, 13.4, 16	9.6

In this research, mandarin peel powder (MPP) was used to determine its effect on the filtration properties of drilling mud and particularly on clay swelling in bentonite-based drilling mud. The main objective of the presented research was to determine whether and to what extent the particle size of the MPP affects the rock swelling properties during interaction with drilling mud. The novelty of this research is to determine the effect of MPP particle size (less than 0.10 mm, and from 0.10 to 0.16 mm) on filtration properties (API and PPT) and clay swelling at room temperature and 90 °C.

2. Materials and Methods

The effects of adding mandarin peel powder to a bentonite-based mud on filtration properties and clay swelling was performed at the Drilling Fluid Laboratory of the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb.

2.1. Preparation of Powder from Mandarin Peel

Figure 2 shows the whole procedure for the preparation of MPP. First, the mandarin peels were dried in an oven for 2 days at 90 °C to completely dehydrate the source material (Figure 2a). After dehydration, the peel was ground in a blender to obtain a fine powder (Figure 2b). The MPP was then sieved through two sieves (the openings of the sieves were 0.10 and 0.16 mm), thus dividing it into two groups regarding particle size: from 0.10 to 0.16 mm, and less than 0.10 mm (Figure 2c).

To gain insight into the size of the MPP particles after grinding and sieving, micrographs were taken with an FE-SEM Mira II LMU, Tescan at the University of Zagreb, Faculty of Textile Technology. Figure 3 (left) shows SEM images of MPP with particles less than 0.10 mm. The particles were irregularly shaped and had a wide range of sizes, although they were all smaller than 0.10 mm. Figure 3 (right) shows a SEM image of MPP containing particles from 0.10 to 0.16 mm. These particles were also irregularly shaped, and some of them were elongated and longer than 0.16 mm, but due to their smaller thickness, they still fit through the openings of the sieve.

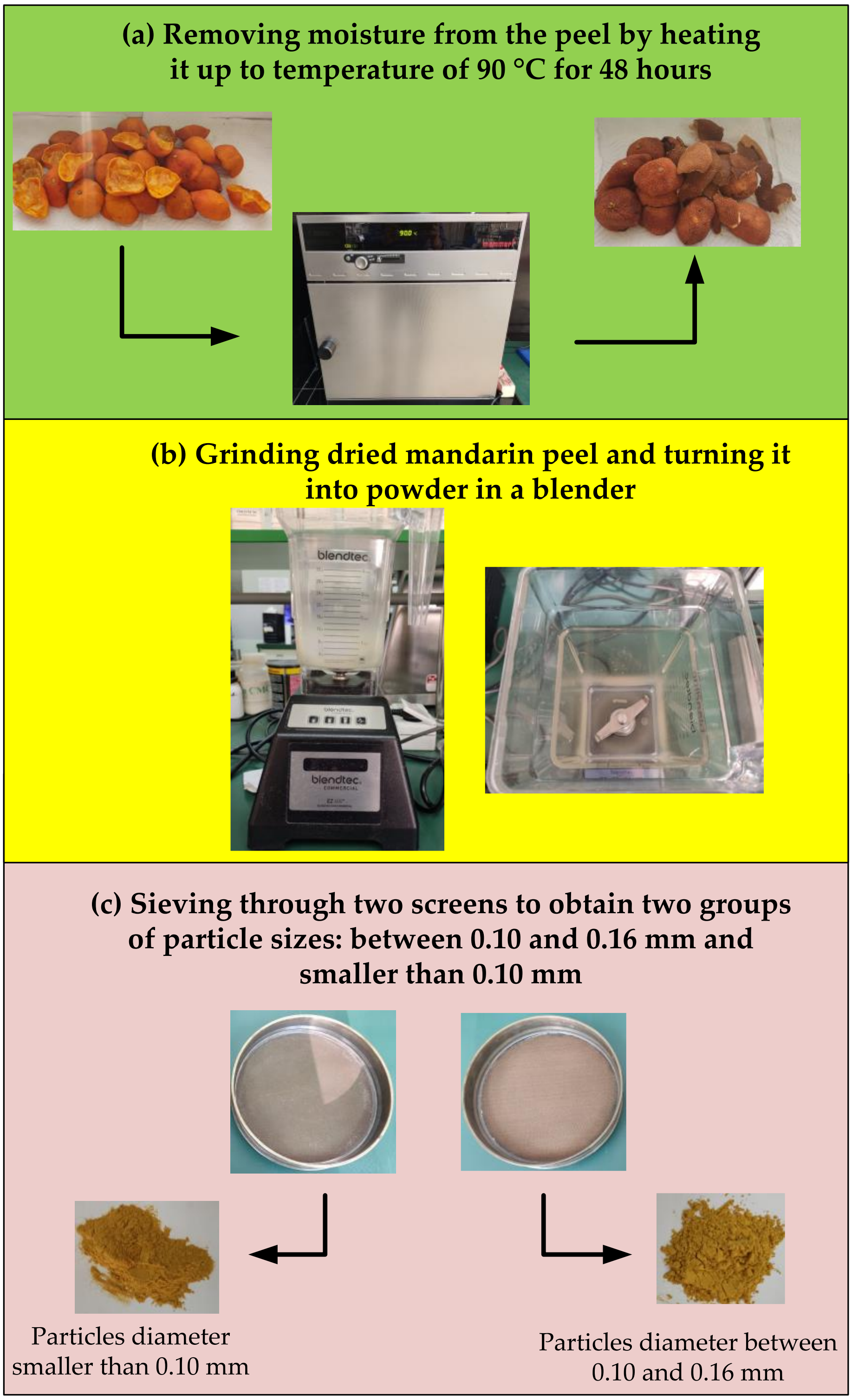

Figure 2. Preparation of Mandarin Peel Powder.

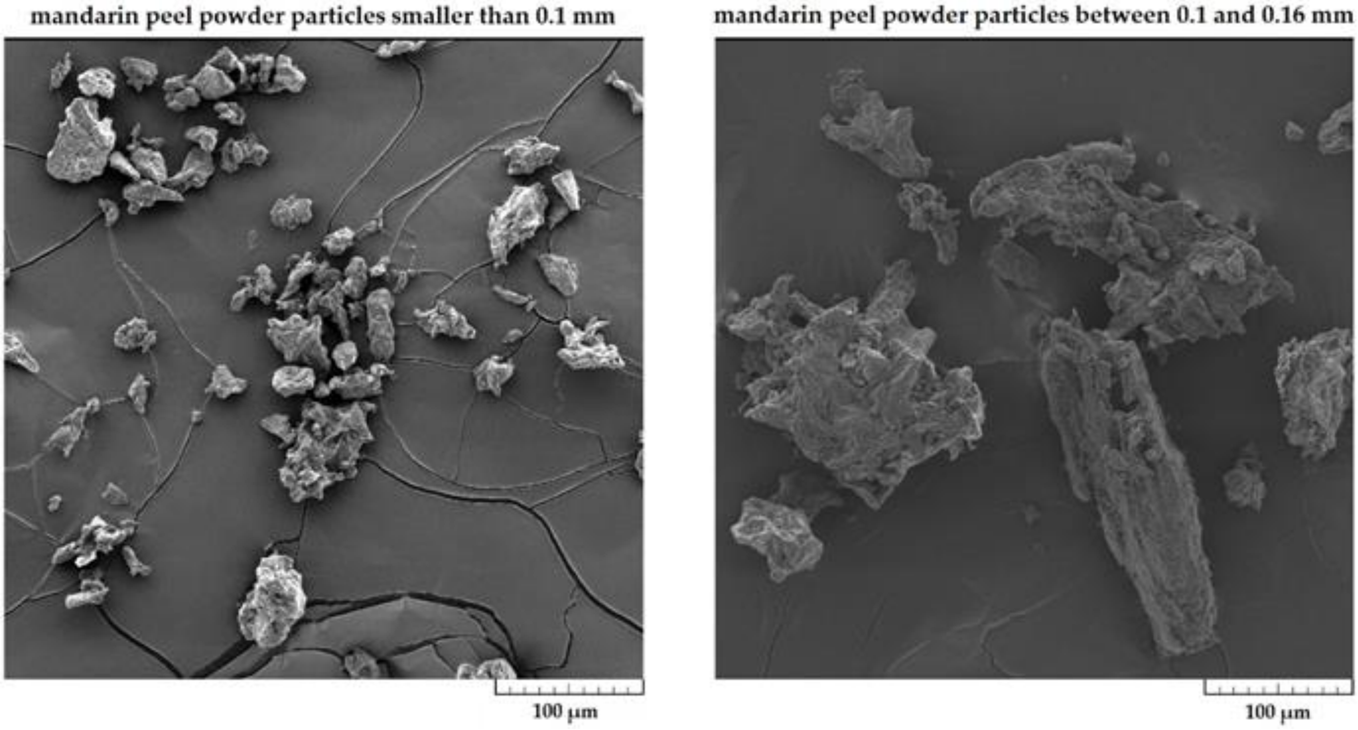

Figure 3. SEM images of MPP containing particles (**left**) less than 0.10 mm and (**right**) from 0.10 to 0.16 mm.

Laboratory tests showed that these two groups of particle sizes influenced the filtration properties and swelling of the quartz–bentonite pellets.

2.2. Preparation of Quartz–Bentonite Pellets

The preparation of quartz–bentonite pellets is shown in Figure 4. A mixture of 6 g of bentonite and 6 g of quartz (Figure 4a) was placed in a compactor cell (Figure 4b), which was then subjected to pressure of 41.36 MPa (6000 psi), which remained constant in the compactor for 30 min according to the manufacturer's instructions (Figure 4c). At the end of compression time, the swelling of the prepared pellet (Figure 4d) was measured using a linear swell meter. The pressure at which the samples were compressed (41.36 MPa) was determined as a function of the type of clay formation that the specific pellets simulate, and the conditions to which the clay was subjected in the subsurface. Compression pressure can be identified as geostatic pressure applied on the clay formation at the considered depth. Assuming an average rock density of 2300 kg/m^3, it is possible to calculate the geostatic pressure affecting the clay formation at a given depth. Therefore, compression pressure of 41.36 MPa (6000 psi) was selected because the objective of this study was to determine the effect of water-based drilling mud containing mandarin powder on the swelling properties of soft clay formations which are located at relatively shallow depths. The selected compression pressure value corresponds to the geostatic pressure value at a depth of about 1800 m.

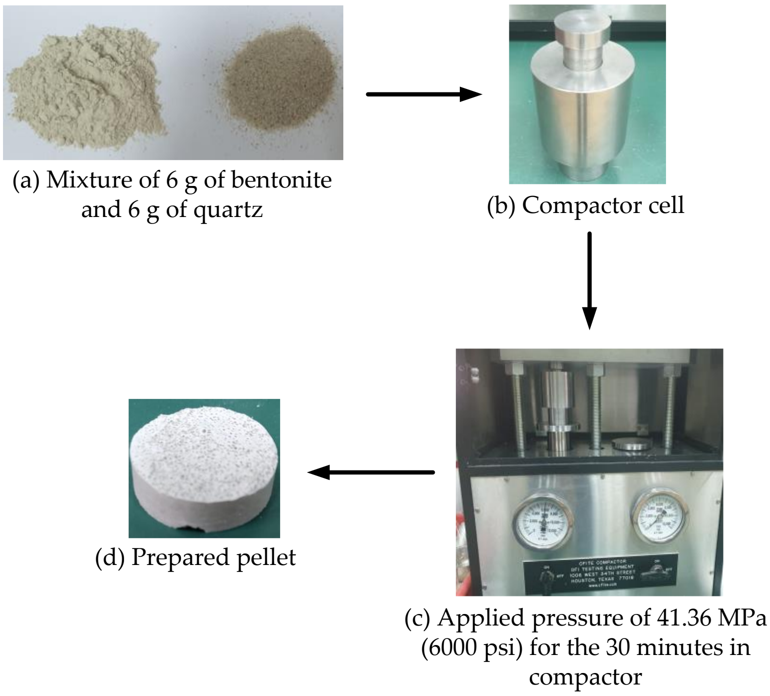

Figure 4. Preparation of quartz–bentonite pellets.

2.3. Preparation of Drilling Mud

All tested drilling-mud samples were prepared in accordance with the American Petroleum Institute Standards, API Specifications 13A and API 13B-1 [44]. To determine the effects of the adding MPP on filtration properties and clay swelling, nine drilling mud samples were prepared and subjected to laboratory testing:

- bentonite-based drilling mud (BM);
- four drilling mud samples containing different concentrations of MPP with particle size of less than 0.1 mm (marked A1–A4);
- four drilling mud samples containing different concentrations of MPP with particle size from 0.1 to 0.16 mm (marked B1–B4).

In 1000 mL of water, 60 g of bentonite was added and stirred for 20 min. To adjust the pH, 1 g NaOH was added, and bentonite-based drilling mud (BM) was prepared. To examine the effect of the particle size and its concentration on filtration properties and clay swelling, eight mud samples were tested with MPP (Table 2).

Table 2. Composition of tested drilling-mud samples which contain MPP.

Tested Mud	Mandarin Peel Particle Size	Mandarin Peel Powder Concentration, % by Volume of Water
A1	Less than 0.1 mm	**0.5**
A2		**1**
A3		**1.5**
A4		**2**
B1	From 0.1 to 0.16 mm	**0.5**
B2		**1**
B3		**1.5**
B4		**2**

2.4. Laboratory Test Equipment and Test Procedures

The used equipment and testing procedures are shown in Figure 5.

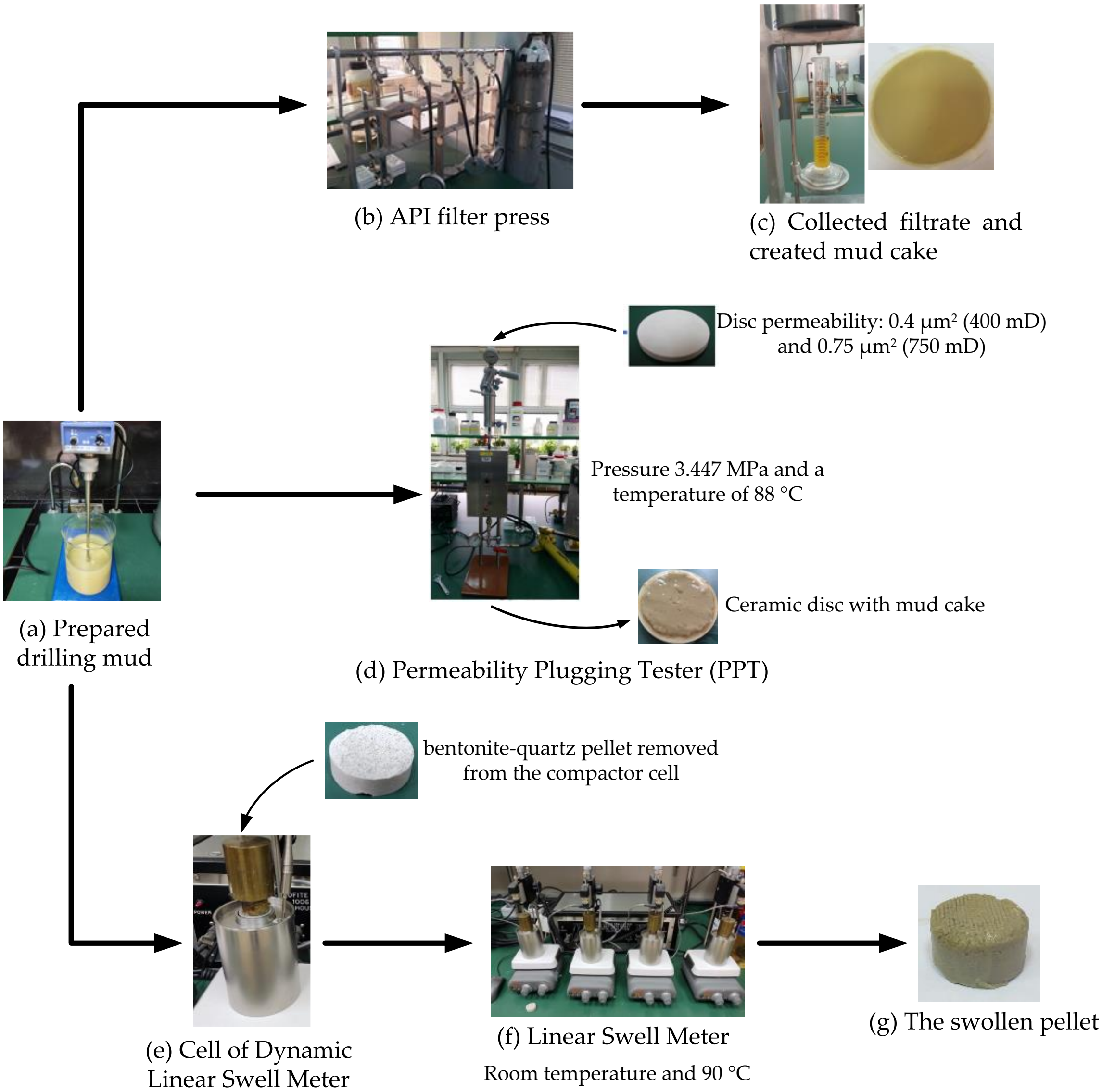

Figure 5. Used equipment and test procedures.

The prepared drilling mud (Figure 5a) was poured into the cell of an API filter press (Figure 5b), and pressure of 0.6895 MPa (100 psi) was applied for a period of 30 min. The filtrate volume extracted from the drilling mud through a filter paper (Whatman No. 50, filter area 45.8 cm^2) was collected in a laboratory beaker, while a mud cake was formed on the paper (Figure 5c). The collected filtrate volume is expressed as API filtration.

The capability of drilling mud to plug pores in a ceramic disc was determined using a permeability plugging tester (PPT) (Figure 5d) and ceramic discs with permeabilities of 0.4 μm^2 (400 mD) and 0.75 μm^2 (750 mD). The tests were performed at a differential pressure of 3.447 MPa and a temperature of 88 °C. During the test, the filtrate was collected in a measuring cylinder after 7.5 min and after 30 min. According to the manufacturer's instructions, to calculate PPT filtration, the collected volume after 30 min must be multiplied by 2 (Equation (1)), while the volume of collected fluid before the formation of a drilling mud cake (spurt loss) is calculated by using Equation (2) [45]:

$$\text{PPT filtrate volume} = 2 \cdot V_{30} \quad (1)$$

$$\text{Spurt loss} = 4 \cdot V_{7.5} - 2 \cdot V_{30} \quad (2)$$

where PPT filtrate volume, mL; $V_{7.5}$, fluid volume collected after 7.5 min, mL; V_{30}, fluid volume collected after 30 min, mL; spurt loss, fluid volume collected before forming a drilling mud cake, mL.

To determine their swelling, the bentonite–quartz pellets were removed from the compactor cell after the compression time of 30 min had elapsed, and placed in the dynamic linear swell meter cell (Figure 5e). The swelling test for each pellet in the selected drilling mud was designed and run for 24 h in the linear swell meter (Figure 5f). In the first case, the swelling of the pellets was determined at room temperature. To determine the effect of temperature on pellet swelling, in the second case, pellet swelling at 90 °C was determined. After 24 h, the swollen pellet was removed from the cell of the dynamic linear swell meter (Figure 5g).

3. Results

Table 3 shows the results of API filtration measurements for the nine tested mud samples. From the presented results, it can be concluded that API filtration decreased with the increasing concentration of MPP. A significant reduction in filtration (from 18 to 13.5 mL) was observed by adding MPP particles less than 0.10 mm at the smallest tested concentration of 0.5% by volume of water (A1), while a significant reduction was achieved at a concentration of 1% by volume of water (B2) by adding larger particles from 0.1 to 0.16 mm (from 18 to 13 mL). The largest decrease in API filtration was gained for larger MPP particles ranging in size from 0.1 to 0.16 mm, added at a concentration of 2% by volume of water (B4), and was 10 mL compared to the measured API filtration of the base mud (18 mL). The thickness of the mud cake, regardless of the concentration of MPP, was slightly decreased by the addition of MPP in comparison with the thickness of the mud cake measured with BM (1.5 mm).

Table 3. Influence of adding MPP on API filtration [46].

Drilling Muds								
BM	**A1**	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**
Mandarin peel powder concentration (%) by volume of water								
0	**0.5**	**1**	**1.5**	**2**	**0.5**	**1**	**1.5**	**2**
API filtration (mL)								
18	13.5	13.5	11.5	11.5	16	13	10.5	10

A certain amount of mandarin powder obtained from mandarin peel dissolved in water [47], which led to an increase in the viscosity of the filtrate, contributing to a decrease in filtration value. In addition, the MPP was assumed to plug the pores in the mud cake, further reducing filtration. Figure 6 shows SEM images of the mud cakes obtained after API filtration of base mud (BM), and two mud samples containing different sizes of MPP at a concentration of 2% by volume of water (A4 and B4 mud samples).

Figure 6 shows the relief surfaces of the mud cake without the indicated pores. It can be seen that for BM the surface is quite uniform with no significant change in texture, while for muds containing MPP, larger accumulations are observed over the entire surface, which are presumably mandarin particles filling small pores in the created mud cake, resulting in a significant decrease in API filtration values.

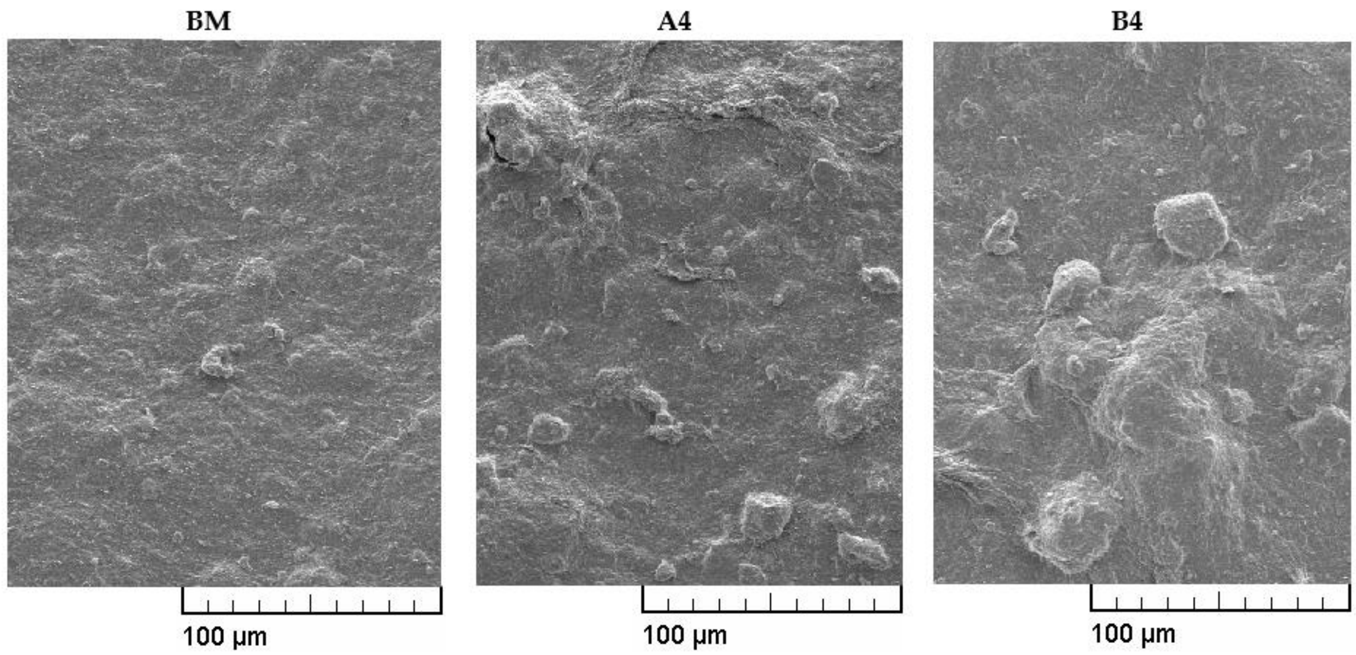

Figure 6. SEM images of mud cakes obtained after API filtration of BM (A4 and B4).

Table 4 summarizes the data of the PPT filtration measurements for both mud samples containing 1% (A2 and B2) and 2% (A4 and B4) of MPP by volume of water.

Table 4. Influence of adding MPP on PPT filtration.

Differential Pressure—3.447 MPa Temperature—88 °C										
Disc permeability	**0.4 µm^2 (400 mD)**					**0.75 µm^2 (750 mD)**				
Drilling mud	BM	A2	A4	B2	B4	BM	A2	A4 [46]	B2	B4 [46]
$V_{7.5}$, mL	15	8	7.5	9.5	7	17	12.5	8	10.5	6
V_{30}, mL	26	15	13	16	12	26	18.5	11	17.5	10
PPT filtrate volume, mL	52	30	26	32	24	52	37	22	35	20
Spurt loss, mL	8	2	4	6	4	16	13	10	7	4

The results for filtration through a 0.4 µm^2 (400 mD) ceramic disc showed a significant decrease in PPT filtrate volume after 30 min for mud A2 (30 mL) containing MPP with a size less than 0.10 mm at a concentration of 1% by volume of water related to the results obtained for BM (52 mL), while twice the concentration of MPP (2% by volume of water) does not result in a significantly greater reduction in PPT filtrate volume (mud A4, 26 mL).

For mud containing MPP with particles size from 0.10 to 0.16 mm, the PPT filtration volume after 30 min for mud containing MPP at a concentration of 1% by volume of water (B2) was similar (32 mL) to mud containing particles less than 0.10 mm (30 mL). At a concentration of 2% by volume of water (B4), PPT filtration was similar (24 mL) to mud containing particles less than 0.10 mm (26 mL).

Spurt loss is significantly lower for mud samples containing MPP less than 0.10 mm in size for both tested concentrations (A2 and A4) (2 and 4 mL) compared to those measured with BM (8 mL). For mud samples containing particles from 0.10 to 0.16 mm, at a concentration of 1% by volume of water (B2), spurt loss decreased in relation to BM, but was still slightly higher (6 mL) than the values obtained for mud samples containing particles less than 0.10 mm (A2 and A4). At a concentration of 2% by volume of water (B2), spurt loss was considerably lower (4 mL) in comparison to values measured with BM (8 mL).

Filtration through a 0.75 μm^2 (750 mD) ceramic disc showed a significant decrease in filtration volume after 30 min for mud containing MPP less than 0.10 mm at a concentration of 1% by volume of water (A2) (37 mL), related to values measured with BM (52 mL). In contrast to the measurement through a 0.4 μm^2 (400 mD) ceramic disc, increasing the concentration to 2% by volume of water significantly reduced PPT filtration (22 mL with A4). For mud samples containing particles from 0.10 to 0.16 mm, a similar trend was observed as that for mud samples containing particles less than 0.10 mm, with a slightly greater decrease in the value of PPT filtration (35 and 20 mL (B muds) compared to 37 and 22 mL (mud samples A)).

Spurt loss was significantly lower for mud samples containing MPP less than 0.10 mm in size at a concentration of 2% by volume of water (A4) (10 mL) compared to values measured with BM (16 mL). For muds containing particles from 0.10 to 0.16 mm, a similar trend was observed as for muds containing particles smaller than 0.10 mm, with a slightly larger decrease in the value of spurt loss (7 and 4 mL (mud samples B)) compared to 13 and 10 mL (A muds)).

Figure 7 shows the swelling of the pellets in the base mud (BM) and in mud samples with added MPP (particles less than 0.1 mm) within 2 and 24 h (mud samples A1–A4) at room temperature.

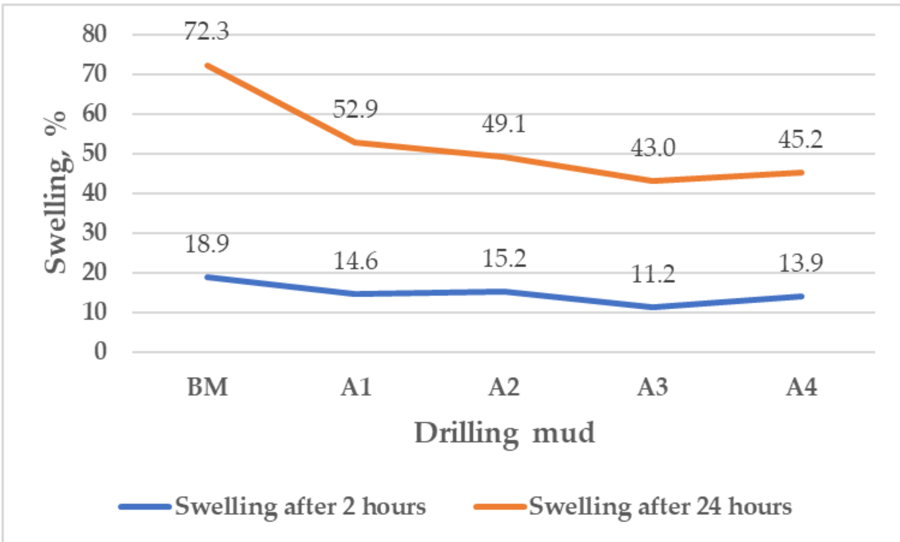

Figure 7. Pellet swelling in base mud and in mud with added MPP (particles less than 0.1 mm) within 2 and 24 h at room temperature.

After 2 h, the swelling of the pellets in the different formulations of mud A was reduced regardless of the concentration of MPP, and ranged from 11.2% to 15.2% compared to the swelling of the pellets in the base mud (18.9%). After 24 h, pellet swelling was also reduced regardless of MPP concentration, and ranged from 43% to 52.9% compared to pellet swelling in the base mud (72.3%). With the addition of MPP, pellet swelling was 52.9% at the lowest tested concentration of 0.5% by volume of water (A1), while increasing the concentration up to 2% did not express the same intensity of pellet-swelling decrease. Moreover, a slight increase of 2.2% in pellet swelling (from 43% (A3) to 45.2% (A4)) was observed after the addition of MPP at a higher concentration than 1.5% by volume of water.

Figure 8 shows the swelling of the pellets in the base mud (BM) and in muds with added MPP (particles from 0.10 to 0.16 mm) within 2 and 24 h (mud samples B1–B4) at room temperature.

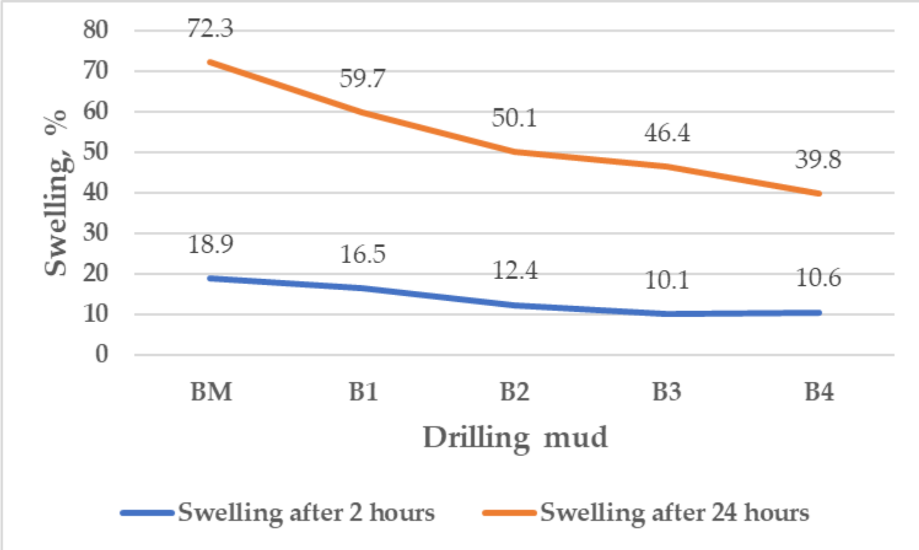

Figure 8. Pellet swelling in base mud and in mud with added MPP (particles from 0.1 to 0.16 mm) within 2 and 24 h at room temperature.

After 2 h, the swelling of the pellets in the different formulations of mud B was reduced regardless of the concentration of MPP and ranged from 10.1% to 16.5% compared to the swelling of the pellets in the base mud (18.9%). After 24 h, pellet swelling was also reduced regardless of the concentration of MPP, and ranged from 39.8% to 59.7% compared to pellet swelling in the base mud (72.3%). When MPP was added at a concentration of 0.5% by volume of water (B1), the measured swelling was 59.7%. A concentration of MPP of 1% by volume of water and above is required to significantly reduce pellet swelling, ranging from 50.1% for mud B2 to the best result (39.8%) obtained for a mud containing 2% of MPP by volume of water (B4).

Figure 9 shows the swelling of the pellets in the base mud (BM) and in mud with added MPP (particles less than 0.10 mm) within 2 and 24 h (mud samples A1–A4) at 90 °C.

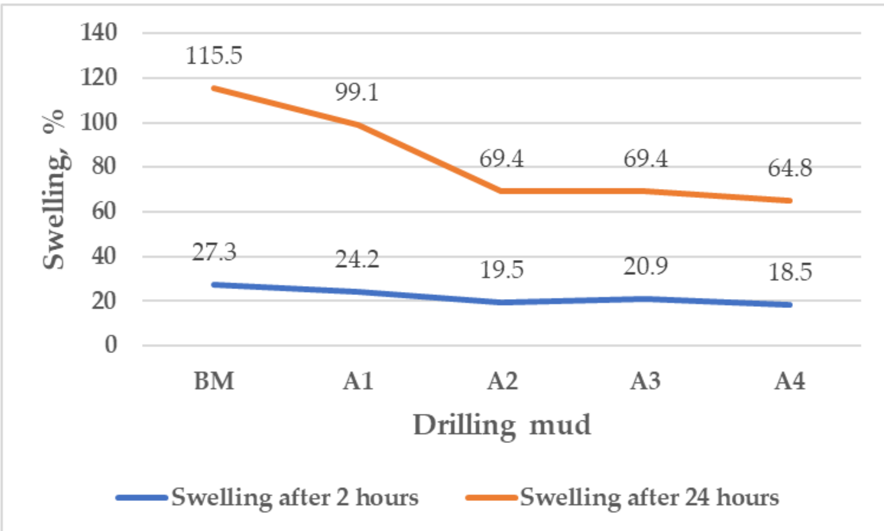

Figure 9. Pellet swelling in base mud and in mud with added MPP (particles less than 0.1 mm) within 2 and 24 h at 90 °C.

After 2 h, the swelling of the pellets was lower regardless of the concentration of MPP, ranging from 18.5% to 24.2% compared to the swelling of the pellets in the base mud (27.3%). After 24 h, the swelling of the pellets was also decreased regardless of the concentration of the MPP, and ranged from 64.8% (A4) to 99.1% (A1) compared to the swelling in the base mud (115.5%). Increasing the concentration of MPP from 0.5% (A1) to 1% by volume of water (A2), pellet swelling continued to decrease (from 99.1% (A1) to 69.4% (A2)), but this trend did not continue with the same intensity with a further increase in MPP concentration, so the pellet swelling was 69.4% (A3) and 64.8% (A4).

Figure 10 shows pellet swelling in the base mud (BM) and in muds with added MPP (particles from 0.10 to 0.16 mm) within 2 and 24 h (mud samples B1–B4) at 90 °C.

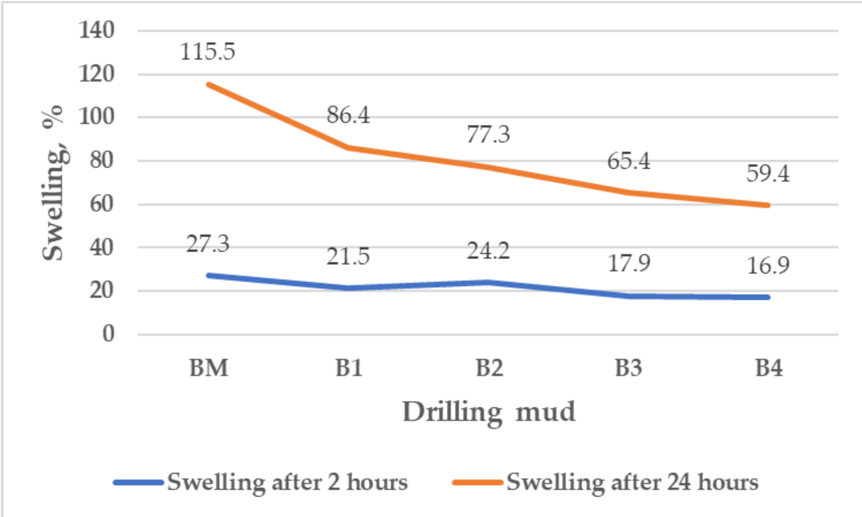

Figure 10. Pellet welling in base mud and in mud with added MPP (particles from 0.10 to 0.16 mm) within 2 and 24 h at 90 °C.

After 2 h, the swelling of the pellets in the different formulations of mud B was reduced regardless of the concentration of MPP, and ranged from 16.9% (B4) to 24.2% (B2) compared to the swelling of the pellets in the base mud (27.3%). After 24 h, the swelling of the pellets also decreased regardless of the concentration of MPP, and ranged from 59.4% (B4) to 86.4% (B1) compared to the swelling of the base mud (115.5%). As the concentration of MPP increased, the swelling of the pellets continuously and significantly decreased, from 86.4% (B1) to 59.4% (B4).

4. Discussion

To determine the effect of MPP on filtration properties and pellet swelling, all results were compared. From the data shown in the Table 5, reduction in API filtration was evident for all tested mud samples relative to API filtration measured with the base mud (BM), expressed as a percentage.

Comparing measured API filtration results with both particle sizes at the same concentrations of MPP, at higher concentrations (1% by volume of water and above) better results were obtained, with powder having larger particles (from 0.10 to 0.16 mm), while at low concentrations (0.5% by volume of water), better results were achieved with MPP having smaller particles than 0.10 mm.

Regardless of the permeability of the disc used in the tests (0.4 or 0.75 μm^2), a positive effect of the addition of mandarin powder on the PPT filtration of the mud was observed, since its value decreased significantly in all cases compared to the values obtained with the base mud (BM).

A comparison of PPT filtration results measured with both particle sizes at the same concentrations of MPP through a 0.4 μm^2 (400 mD) ceramic disc shows that, at a concentration of 1% by volume of water, slightly better results were obtained with MPP with particles less than 0.10 mm (42.31% compared to 38.46%), while at a concentration of 2% by volume of water, slightly better results were obtained with MPP with particles from 0.10 to

0.16 mm (53.85% compared to 50%). At a concentration of 1% by volume of water, results of spurt loss for mud samples containing MPP particles less than 0.10 mm were significantly better (75% reduction) than the results for mud samples containing MPP particles from 0.10 to 0.16 mm (25%). At a concentration of 2% by volume of water, regardless of MPP size, the reduction in spurt loss was similar (50%).

Table 5. Decrease in API filtration, PPT filtration, and spurt loss for all tested mud samples in regard to base mud (BM).

Drilling Mud							
A1	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**
Reduction in API filtration (%)							
25	25	36	36	11	28	42	44
Reduction in PPT filtration (%) through 0.4 μm^2 (400 mD) disk							
-	42.31	-	50	-	38.46	-	53.85
Reduction in PPT filtration (%) through 0.75 μm^2 (750 mD) disk							
-	28.85	-	57.69	-	32.69	-	61.54
Reduction in spurt loss volume (%) through 0.40 μm^2 (400 mD) disk							
-	75	-	50	-	25	-	50
Reduction in spurt loss volume (%) through 0.75 μm^2 (750 mD) disk							
-	18.75	-	37.5	-	56.25	-	75

Comparing the PPT filtration results measured with both particle sizes at the same concentrations of MPP through a 0.75 μm^2 (750 mD) ceramic disc, it is shown that slightly better results were obtained with MPP particles from 0.10 to 0.16 mm (32.69% compared to 28.85% at a concentration of 1% by volume of water and 61.54% compared to 57.69% at a concentration of 2% by volume of water). The same trend was observed in determining the value of spurt loss, with significantly better results obtained with powders with particles from 0.10 to 0.16 mm (56.25% related to 18.75% at a concentration of 1% by volume of water and 75% related to 37.75% at a concentration of 2% by volume of water).

Figure 11 shows the pellet swelling reduction in mud samples with added MPP within 24 h related to the pellet swelling measured with the base mud at room temperature and 90 °C, expressed as a percentage.

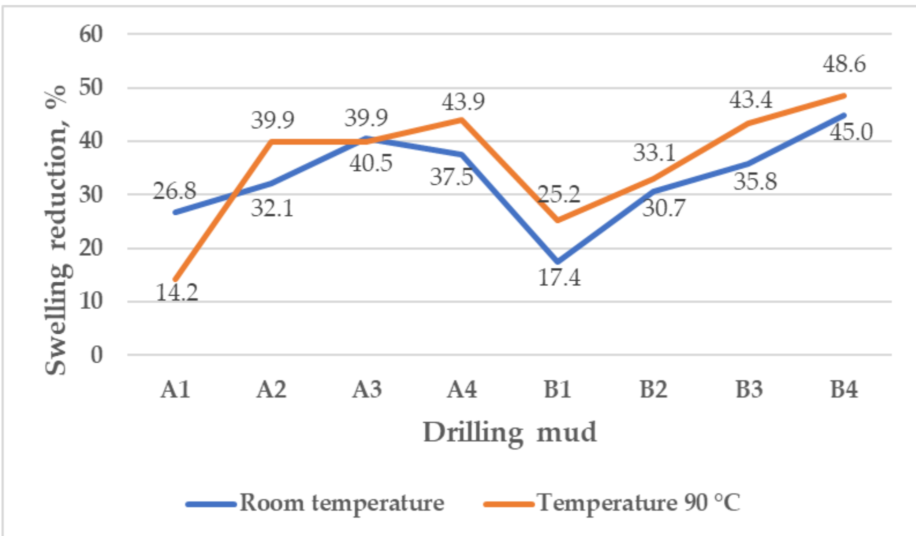

Figure 11. Pellet swelling reduction in different mud samples with added MPP in regard to base mud (BM) within 24 h.

Regardless of the concentration of MPP and particle size, a decrease in pellet swelling between 17.4% (B1) and 45% (B4) was observed at room temperature, and a decrease in swelling between 14.2% (A1) and 48.6% (B4) was determined at 90 °C. When the concentration of MPP increased, the reduction in pellet swelling increased for mud samples containing particles from 0.1 to 0.16 mm (mud samples B1–B4), from 17.4% (B1) at a concentration of 0.5% by volume of water up to 45% measured with mud B4 containing 2% by volume of water at room temperature. At 90 °C, results were similar to those measured at room temperature, but the reduction in pellet swelling was slightly greater, from 25.2% (B1) to 48.6% (B4).

At room temperature, a similar trend was observed in measurements with mud containing MPP particles less than 0.10 mm (mud samples A1–A4), with one exception. The greatest reduction in swelling was observed for mud A3, containing MPP at a concentration of 1.5% by volume of water (40.5%). However, at a concentration of 2% by volume of water (A4), the reduction in pellet swelling was less than that (37.5%), indicating that it is not necessary to increase the concentration of MPP beyond 1.5% by volume of water. At 90 °C, the reduction in pellet swelling at a concentration of MPP of 1% by volume of water or more was similar (from 39.9% to 43.9%); at a low concentration of 0.5% by volume of water (A1; 14.2%), a slightly lower value of reduction in pellet swelling was observed compared to the reduction measured at room temperature (26.8%).

Although this research shows that the best results were obtained at higher concentrations of MPP (1.5% and 2% by volume of water), the effects on other properties of the drilling mud, especially rheology, need to be further studied to determine the potential of these muds for adequate wellbore cleaning. Considering that satisfactory results were also obtained at lower concentrations (up to 1% by volume of water), it is necessary to select those concentrations that had a satisfactory effect on API filtration and shale swelling, but that also present other adequate properties to allow for the wellbore to be safely drilled while reducing the negative environmental impact of drilling mud.

5. Conclusions

On the basis of laboratory tests, the following conclusions can be drawn:

- MPP added to water-based mud reduces API filtration, PPT filtration, spurt loss, and pellet swelling regardless of particle size and concentration;
- the best results were obtained by adding MPP with particles from 0.10 to 0.16 mm at a concentration of 2% by volume of water;
- a 44% reduction in API filtration was achieved with mud B4 containing MPP particles from 0.10 to 0.16 mm at a concentration of 2% by volume of water;
- a 61.54% reduction in PPT filtration through a 0.75 μm^2 (750 mD) ceramic disk was achieved with mud B4 containing MPP particles from 0.10 to 0.16 mm at a concentration of 2% by volume of water;
- a 53.85% reduction in PPT filtration through a 0.4 μm^2 (400 mD) ceramic disk was achieved with mud B4 containing MPP particles from 0.10 to 0.16 mm at a concentration of 2% by volume of water;
- a 45% reduction in pellet swelling after 24 h was measured with mud B4 containing MPP particles from 0.10 to 0.16 mm at a concentration of 2% by volume of water at room temperature;
- a 48.6% reduction in pellet swelling after 24 h was obtained with mud B4 containing MPP particles from 0.10 to 0.16 mm added at a concentration of 2% by volume of water at 90 °C;
- satisfactory results were obtained up to a MPP concentration of 1% by volume of water;
- the swelling reduction results correlated very well with the API filtration reduction results.

In general, it can be concluded that the addition of MPP to the drilling mud can increase wellbore stability. However, further measurements of the properties of the drilling mud are necessary to determine the optimal concentration that ensures adequate mud properties for the safe drilling of the well.

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The influence of mandarin peel powder on filtration properties and temperature stability of water-based drilling mud

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Abstract

The growing energy demand in the world, as well as the current geopolitical situation, require countries to additional investments in the exploration and production of hydrocarbons from their own sources. This means that companies must develop new fields which have remained undeveloped until now mostly because extremely harsh environment where they are located (deep sea, high temperature, high pressure, heavy oils, etc.). The development of these new fields requires the development and adoption of new technology, among other things, and the development of a temperature-stable drilling fluid system able to fulfil all tasks according to the new technical challenges. Except for the technological challenges, there are also growing concerns related to the influence of the drilling operation on the environment. All of the above encourage the industry to develop new, inexpensive, and environmentally friendly additives which will be able to satisfy all technical and technological requirements and challenges of modern drilling. In the last few years, there has been a growing trend of laboratory research that includes different types of biodegradable waste as a potential additive that can achieve useful properties in mud. In this paper, the influence of mandarin peel powder on the filtration properties of mud after the aging process at elevated temperatures is examined. This eco-friendly additive was added to water-based muds in concentrations of 1% and 2% by volume of water. Laboratory research have shown stable filtration properties of the water-based mud containing mandarin peel powder even after exposing the mud to temperatures higher than 130 °C.

Keywords:

mandarin peel powder; mud; filtration; hot roll process

1. Introduction

The drilling fluid or drilling mud is probably most important and most expensive component of the drilling process, and its main task is removing of the drilling cuttings from the wellbore **(Valizadeh and Nasiri, 2012; Sarah et al., 2016; Gudarzifar et al., 2020)**. Except carrying cuttings from the wellbore to surface, it must fulfil the additional tasks, regardless of drilling mud type. Among others, most important are balancing pore pressure and prevention of reservoir fluid overflow and possible blowout, cooling and lubrication of the drill string and drill bit, prevention of the mud losses by creation of the filter cake on the wellbore wall and supporting weight of the drilling string **(Neshat et al., 2015.; Olise et al., 2017; Ma et al., 2021; Chu and Lin, 2019; Wiśniowski et al., 2020; Wiśniowski et al., 2022; Long et al., 2022)**. Also, in regular drilling conditions, drilling mud density should be high enough to prevent intake of the reservoir fluid into wellbore and below the level that would result with fracturing of the reservoir rock at the same time. Demand for the new energy sources also requires drilling deep, high temperature or extended wells which entails further development of the drilling mud in order to satisfy drilling process in this complex condition **(Huang et al., 2019; Ismail et al., 2020; Chu et al. 2020a; Fayad et al., 2021)**. The drill cuttings removing process also depends on rate of the penetration, and pure wellbore cleaning from excessive drilling cuttings results in spending energy for additional crushing of the drilled cuttings. Unfortunately, temperature increase with the depth results in thermal thinning at many types of drilling mud and causing inadequate wellbore cleaning and consequently slowing down of the drilling process, occurrence of unwanted drilling events (stuck pipe, blowouts or wellbore instability) and therefore questions drilling security as well as assurance of the wellbore isolation by cementation **(Echt and Plank, 2019; Liu et al, 2020; Hamad et al., 2020; Gudarzifar et al., 2020)**.

All the above-mentioned tasks as well as the complex and the unique downhole conditions makes the drilling mud design process technical and engineering demanding **(Yunita et al., 2016)**. Moreover, it should be kept in mind that drilling mud design process includes design more than one drilling mud for the specific well. Although oil companies select water-based drilling mud rather than oil-based drilling, they are aware of the water-based drilling mud deficiencies at elevated temperature. Moreover, numerous research clearly indicate that oil-based mud has a larger stability in the high-temperature and high condition as well as other advantages

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regarding to water-based drilling mud (gives better lubricity, increase wellbore stability, decrease filtrate invasion and formation damage, etc.), but economic and environmental concern have limited their wider application **(Ettehadi, 2021; Khan et al., 2018; Said and El-Sayed, 2018)**. The synthetic-based drilling mud (Esters, Olefin, Ethers, Polyalphaolefins) has lower toxicity compared to the oil-based drilling mud, they can be recycled and exhibit temperature stability problems. Although oil- and synthetic-based drilling muds are initially more expensive than water-based drilling mud, they can reduce overall drilling cost by decreasing some drilling problems, which cannot be solved by using water-based drilling mud **(Sajjadian et al., 2016)**. In the deep offshore drilling range of the wellbore, temperature variation is especially emphasized, and typical range is between 4 °C and 80 °C **(Xie et al., 2021)**. According to **Xie et al. (2021)** common polymers and clays have similar response to the temperature changes and does not fit temperature alteration in deep offshore drilling. According to **Wenjun et al. (2014)** high temperature influences the polymer stability in drilling mud system in two ways. The high temperature can cause removing of the hydrophilic group from the main chain of the polymer and breaking carbon-carbon bond or crosslinking of the polymer because of unsaturated bond and active group. Except high temperature condition, salts (of specific type and concentration) have great influence on polymer stability as well as presence of the dissolved oxygen **(Ma et al., 2021)**. Some authors found that adding of antioxidants, formate salts and polyglycols can increase temperature stability of biopolymers within water-based drilling mud system and prevent acid-catalysed hydrolysis and oxidation-reduction reaction as main mechanisms responsible for thermal degradation of biopolymers **(Valizadeh and Nasiri, 2012; Akpan, et al., 2018)**. The elevating temperature can influence drilling mud viscosity through process of the high temperature thinning, thickening or solidification causing change in mud fluidity **(Fuhua et al., 2012)**. Better stability of the water-based drilling mud in high-temperature and high-saline environment can be achieved using synthetic polymer **(Hamad et al., 2020; Chu and Lin, 2019)**. The molecular flexibility of the synthetic polymers used as additive for regulation of the rheological and filtration properties of the water-based drilling mud, can assure thermal stability of the water-based drilling mud and sustainability of its properties **(Chu and Lin, 2019)**. **Yunita et al. (2016)** tried to improve stability and overall performance of water-based drilling mud at elevated temperature by adding non-ionic and anionic surfactants. Obtained results from laboratory research clearly indicate that adding surfactant can stabilize and even improve rheological properties after 16 hours of hot rolling process at elevated temperature and decrease filtration up to 41,3%. Except additives for rheological and filtration properties, some other additives, such as shale inhibitors (KCl or NaCl) also can be affected by increased temperature but to a lesser extent **(Liu et al, 2020)**. One of the shale inhibitors with the great potential, polyamine, have the temperature stability on less than 120 °C and elevation temperature cause easy desorption of inhibitor from clay surface **(Chu et al., 2020b)**. In this situation, new polymers such as PGBA (P(AMPS-MBA)-g-P(Am-DEAm)) ensure temperature stability of drilling mud rheological properties over the whole range of the wellbore temperature. **Liu et al. (2020)** developed and tested new bentonite based drilling muds by adding poly(Sodium 4-Styrenesulfonate) to the base bentonite mud, and the new formulation exhibits superior rheological and filtration properties over regular bentonite drilling muds with hydroxyethyl cellulose (HEC) and carboxymethyl cellulose (CMC). They concluded that adding poly(Sodium 4-Styrenesulfonate) prevent aggregation of the bentonite particles and therefore drilling mud keep good properties even after hot rolling at 200 °C. **Akpan et al. (2018)** investigated influence of the combination of additives on stabilization of the biopolymers (konjac and xanthan gum) at the high temperature, and they found that best biopolymer stabilisation can be achieved by combination of potassium formate, sodium erythorbate and 0.7% polyethene glycol. To overcome water-based drilling mud problems caused by thermal degradation, **Hamad et al. (2020)** added to drilling mud formulation small amount of amphoteric polymer (PEX) which improves both, rheological and filtration properties of the tested water-based drilling mud. **Khan et al. (2018)** researched influence of the carbon nanotubes and zinc oxide nanoparticles on thermal stabilisation of the water-based drilling mud and conclude that carbon nanotubes can promote thermal stability as well as rheological and filtration properties of the tested water-based drilling mud, while this improvement was absent in case of the drilling mud with zinc oxide nanoparticles. The similar positive effect of nanoparticles, in this case bismuth ferrite nanoparticles on rheological and filtration properties of water-based drilling mud, were noticed by **Perween et al. (2018)** in their research. They believed that this positive effect is result of the interaction between nanoparticles and clay particles. **Gudarzifar et al. (2020)** achieved significant improvement/stabilization of water-based drilling mud properties, especially at elevated temperatures by adding nanocomposite material (graphene oxide nanosheet, polyacrylamide and graphene oxide nanosheet/polyacrylamide nanocomposite) in drilling mud formulation.

The proper drilling mud design process includes conduction of the laboratory test at simulated downhole conditions. Some authors are questioning conventional method for researching influence of the temperature on the drilling mud properties, especially for rheological properties measurements. In its research, **Echt and Plank (2019)** point to a fact that hot rolling of the drilling mud, with an aim of determining of the drilling mud thermal stability and consequently carrying capacity, can lead researchers to wrong conclusions. To better determination of the in situ rheological properties of the drilling muds some authors such as **Ettehadi (2021)** suggest using Discovery Hybrid Rheometer (DHR-II) instead of Fann VG viscometer, and extension of the routine laboratory test according to API standards with additional test such as Freeze-Thaw Cycle test. Although these new recommendations undoubtedly contribute better simulation of the downhole hole condition and give more precise results, most researchers adhere to common testing procedures according to the API standards.

In order to satisfy the increasingly rigorous standards in environmental protection, oil and gas industry is trying to develop the new environmentally friendly drilling mud formulation and additive as well. In the last few years, there has been a growing trend of testing different types of biodegradable waste as a potential additive that can achieve useful properties in mud. The advantage of this type of additive is primarily in reducing the negative impact on the environment, considering that many commercially available additives for water-based mud fall into the category of non-degradable and environmentally hazardous materials **(Zheng et al., 2020)**. One of the possible solutions is using cellulosic agricultural waste material (for example Plant press slag) as additive for preparation of environmentally friendly drilling mud **(Long et al., 2022)**. Despite of the great potential of this idea, additional comprehensive laboratory and filed research are needed to fully understand effect of this waste material as new drilling mud additive at complex downhole condition. Research presented in this paper is a continuation and upgrade of the previous tests on the use of mandarin peel powder, in which the positive properties of this additive on the filtration properties of the mud with a change in the rheological properties within acceptable limits **(Medved et al., 2022a)** and a reduction in the swelling of the clay component were proven **(Medved et al., 2022b)**, which positively affects the stability of the wellbore. The aim of this paper is to prove the resistance of mandarin peel powder in basic and more complex mud compositions to elevated temperatures, that are common in well conditions.

2. Laboratory Research

In order to investigate the influence of this additive under elevated pressure conditions, different mud compositions were subjected to hot roll aging process. Prepared mud samples were sealed in a separate cell and placed inside roller, over an equal period of time. The observed samples are continuously rolled on rotating shafts which simulates the circulation of drilling mud in the well.

2.1. Mandarin Peel Powder Preparation and Laboratory Tests

After collecting the mandarin peel, the first stage in the preparation of this eco-friendly additive is drying in oven at 90°C for two days. The dried mandarin peels are then grounded and sieved through screens with different openings – 0.16 mm opening on the sieve and 0.10 mm opening on the sieve. In this way, the distribution of particle sizes in two groups is obtained (particles smaller than 0.10 mm and from 0.10 mm to 0.16 mm). Through laboratory measurements, it can be determined whether this has any influence on the results of filtration, in addition to the influence of the concentration of this additive in the mud. This is followed by the mud preparation, in accordance with API Specifications 13A and API 13B-1 **(American Petroleum Institute, 2003)**, of a certain composition and pouring into cells that are placed in a roller and heated at an elevated temperature for 16 hours. After the mud aging process is completed, mud is poured into the API filter press cell and the API filtration is measured during 30 minutes. Pressure of 0.6895 MPa (100 psi) was utilized during that period, and the volume of collected filtrate in a laboratory beaker was extracted from the water-based drilling mud through Whatman No. 50 filter paper with filtration area of 45.8 cm^2 (7.1 in^2) located on the bottom of API filter press cell.

Complete process is shown on **Figure 1**. Given that the mud has undergone an aging process at several different temperatures, after measuring the API filtration it can be concluded from the filtrate volume whether the useful properties of this additive are lost at elevated temperatures and what is the temperature limit of mandarin peel powder in the basic mud and muds with a more complex composition.

2.2. Drilling Mud Composition

For this research, mandarin peel powder concentration of 1% and 2% by volume of water was selected in order to determine the filtration of the mud after the aging process, given that in previous research it was determined that a concentration of less than 1% does not give completely satisfying results **(Medved et al., 2022a)**, while a concentration above 2% is too high, given that the mud gels too much and is impossible to mix it during preparation. For every temperature that was determined for hot roll aging of mud samples, five different basic mud compositions were prepared **(Table 1),** and also five more complex drilling mud compositions **(Table 2).** Aging of all prepared drilling muds was conducted at four different temperature values: 75 °C, 100 °C, 125 °C and 150 °C. After the filtration results were analyzed, it was determined that a significant drop in the properties of the mud with added mandarin peel powder occurred at temperatures between 125 °C and 150 °C. In order to obtain more accurate results of the effect of temperature to positive properties of mandarin peel powder in drilling mud, two additional temperature values were added at which the aging of the mud was carried out, on 133°C and 142 °C.

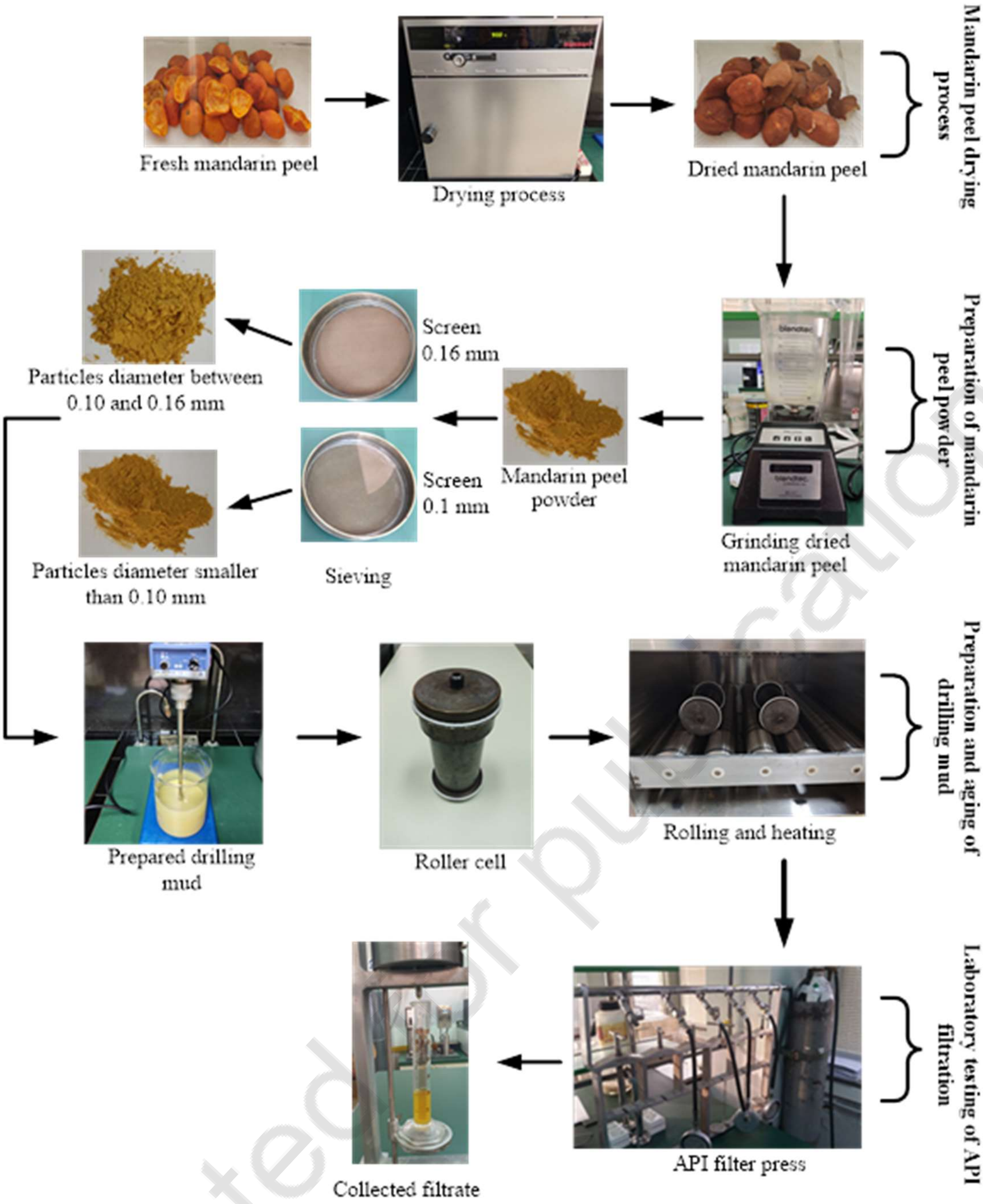


Figure 1: The process of preparing mandarin peel powder and performing API filtration after mud aging

2.2.1. Basic mud Composition

In order to better study the impact of mandarin peel powder on filtration of water-based mud, the basic bentonite-based mud was compared with four other mud compositions in which mandarin peel powder of different particle sizes and concentrations was added. Laboratory research was conducted on two groups of particle sizes - less than 0.10 mm and between 0.10 mm and 0.16 mm, and in two concentrations of added mandarin peel powder, 1% and 2% by volume of water. The mud compositions are listed in **Table 1**. Base mud (Bentonite-based mud) is marked as BM, two drilling muds that contain mandarin peel powder with particles smaller than 0.1 mm are marked as A, and other two drilling muds that contain mandarin peel powder with particles between 0.1 mm and 0.16 mm are marked as B. Each laboratory tested water-based mud was prepared in accordance with the American Petroleum Institute Standards, API Specifications 13A and API 13B-1 **(American Petroleum Institute, 2003)**.

Table 1: Basic water-based drilling mud composition prepared for aging and filtration laboratory tests

Drilling mud mark	Water-Based Drilling Mud Composition			
	Bentonite (g/L)	NaOH (g/L)	Mandarin peel powder concentration (% by volume of water)	Mandarin peel powder particle size (mm)
BM	60	1	-	-
A1	60	1	1	smaller than 0.10
A2	60	1	2	smaller than 0.10
B1	60	1	1	between 0.10 and 0.16
B2	60	1	2	between 0.10 and 0.16

2.2.2. Complex Mud Composition

Although the direct influence of mandarin peel powder on the mud filtration properties can be seen in more detail in the basic mud, one of the aims of this paper is to determine if this eco-friendly additive has any effect on the said property in more complex muds. In this case, PAC R and barite have been added to basic water-based drilling mud. PAC R is modified natural polyanionic cellulosic polymer and barite is barium sulfate material. Barite is heavyweight additive, and its function is to increase the density of the mud in order to increase the hydrostatic pressure, given that the mud is the primary barrier to formation pressure. PAC R is an additive that has a positive effect on the filtration properties of mud and in this laboratory research it was added in recommended concentration, so it is interesting to study whether mandarin peel powder can further improve filtration in the composition of mud that already has an additive for this property. It is also known that bentonite is also used to control filtration, so in this type of more complex mud composition it is much more difficult to improve this property compared to basic mud. The detailed composition of the more complex mud with the indicated markings is shown in **Table 2**. More complex base mud is marked as BMc and it is consisted of bentonite, barite, NaOH and PAC R. Two drilling mud samples that contain all the listed additives with added mandarin peel powder with particles smaller than 0.1 mm are marked as C, and other two drilling muds that contains base mud composition with added mandarin peel powder with particles between 0.1 mm and 0.16 mm are marked as D.

3. Results

3.1. API Filtration Results for Basic Water-Based Drilling Mud with Added Mandarin Peel Powder

Mud aging was done at six different temperatures, and all samples of basic water-based drilling muds were first aged at 75 °C, and final temperature was set at 150 °C. **Figure 2** shows the results of API filtration laboratory tests for the five mud samples after 16 hours hot roll mud aging at temperature of 75 °C, 100 °C, 125 °C and 133 °C.

Table 2: More complex water-based drilling mud composition prepared for aging and filtration laboratory tests

Drilling mud mark	Drilling Mud Composition					
	Bentonite (g/L)	NaOH (g/L)	PAC R (g/L)	Barite (g/L)	Mandarin peel powder concentration (% by volume of water)	Mandarin peel powder particle size (mm)
BMc	60	1	1	40	-	-
C1	60	1	1	40	1	smaller than 0.10
C2	60	1	1	40	2	smaller than 0.10
D1	60	1	1	40	1	between 0.10 and 0.16
D2	60	1	1	40	2	between 0.10 and 0.16

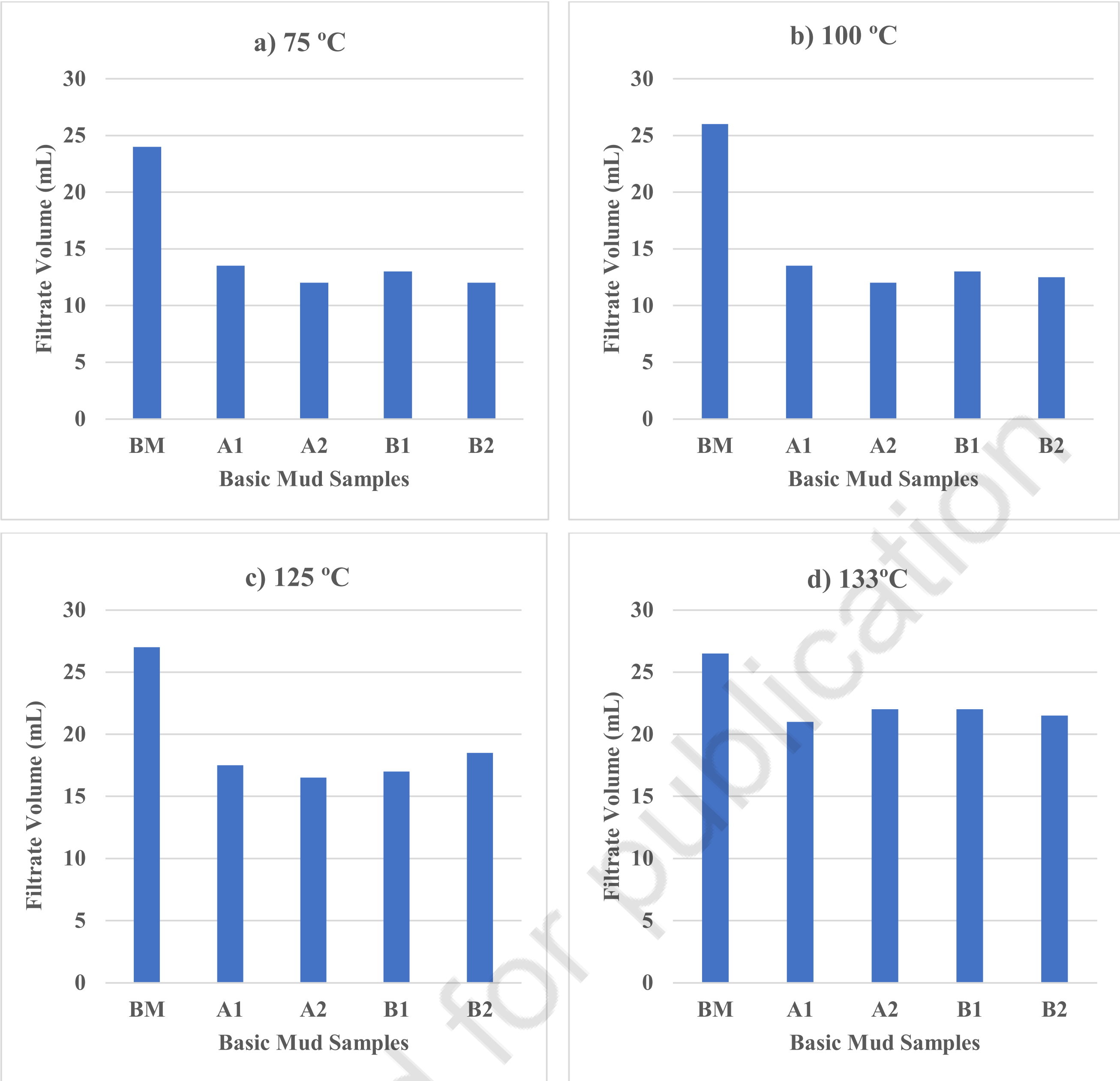


Figure 2: API Filtration results after mud aging process at 75 °C, 100 °C, 125°C and 133°C for basic water-based drilling mud

From the results presented on **Figure 2**, it can be concluded that values of API filtration decreased for every mud sample with added mandarin peel powder in regard to base mud. It is also evident for muds which have concluded aging process up to 100 °C that there is no significant difference between muds into which 1% and 2% of mandarin peel powder was added, i.e. slightly better results were obtained with 2% of added mandarin peel powder. As for the differences in results between the two groups of different particle sizes, insignificant differences were recorded at the same concentration.

For higher temperatures of mud aging process (125 °C and 133 °C), API filtration also decreased for every mud sample with added mandarin peel powder in regard to base mud. The positive influence of this additive on filtration is less pronounced (this especially applies to mud samples that completed the mud aging process at 133 °C) than in the case of muds that have undergone the mud aging process up to a temperature of 100 °C, and there is no significant difference in results between muds into which 1% and 2% of mandarin peel powder was added, and the same applies for differences in results between the two groups of different particle sizes.

Figure 3 shows the results of API filtration laboratory tests for the five mud samples after 16 hours hot roll mud aging at temperature of 142 °C and 150 °C.

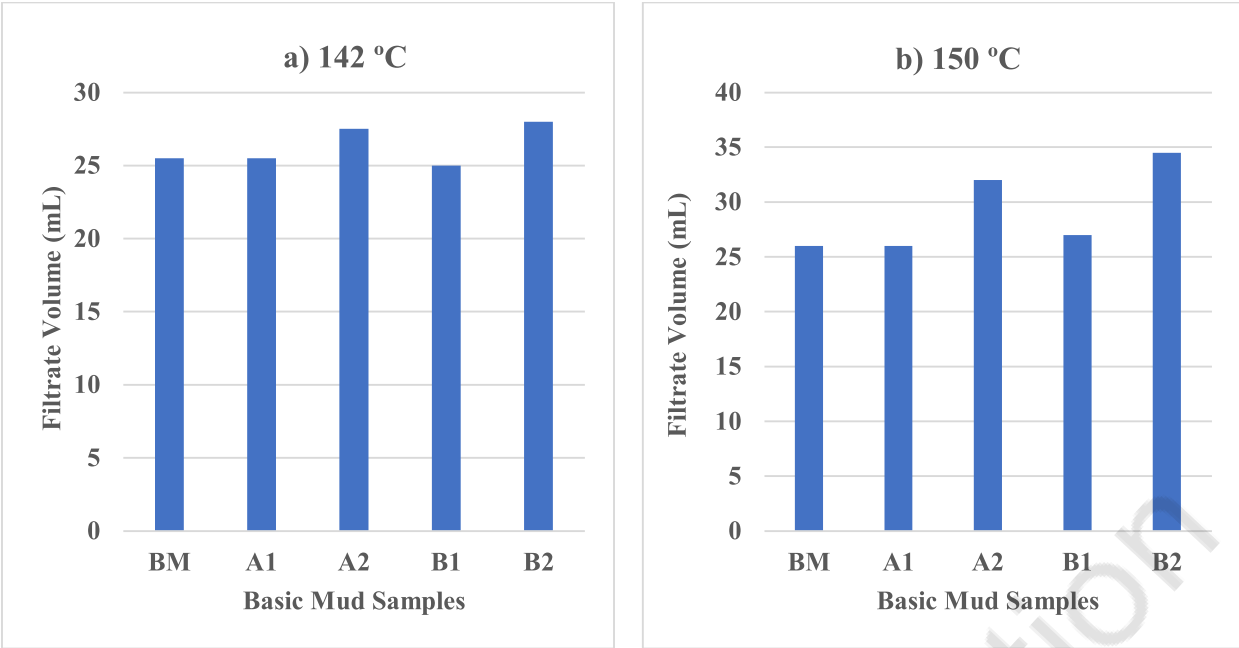
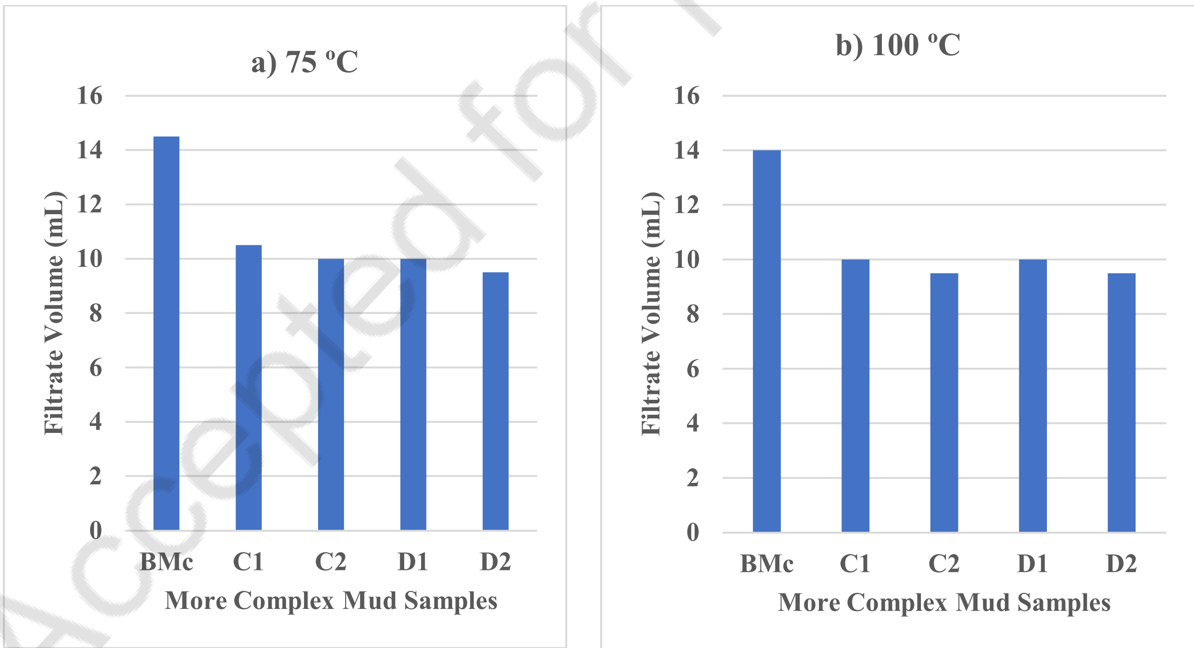


Figure 3: API filtration results after mud aging process at 142 °C and 150 °C for basic water-based drilling mud

From the results presented on this figure, it can be concluded that values of API filtration for mud samples with added mandarin peel powder in concentration of 1% by volume of water remained at the same level as for the base mud, and that concentration of 2% of mandarin peel powder by volume of water even increased filtrate volume in regard to base mud. Again, insignificant differences in results were observed between the two groups of different particle sizes, at the same concentration.

3.2. API Filtration Results for More Complex Water-Based Drilling Mud with Added Mandarin Peel Powder

Mud aging process was completed at six different temperatures at same values as for Basic Water-Based Drilling Mud. **Figure 4** shows the positive effect of added mandarin peel powder on API filtration results for the five mud samples after 16 hours hot roll mud aging at temperature of 75 °C, 100 °C, 125 °C and 133 °C.



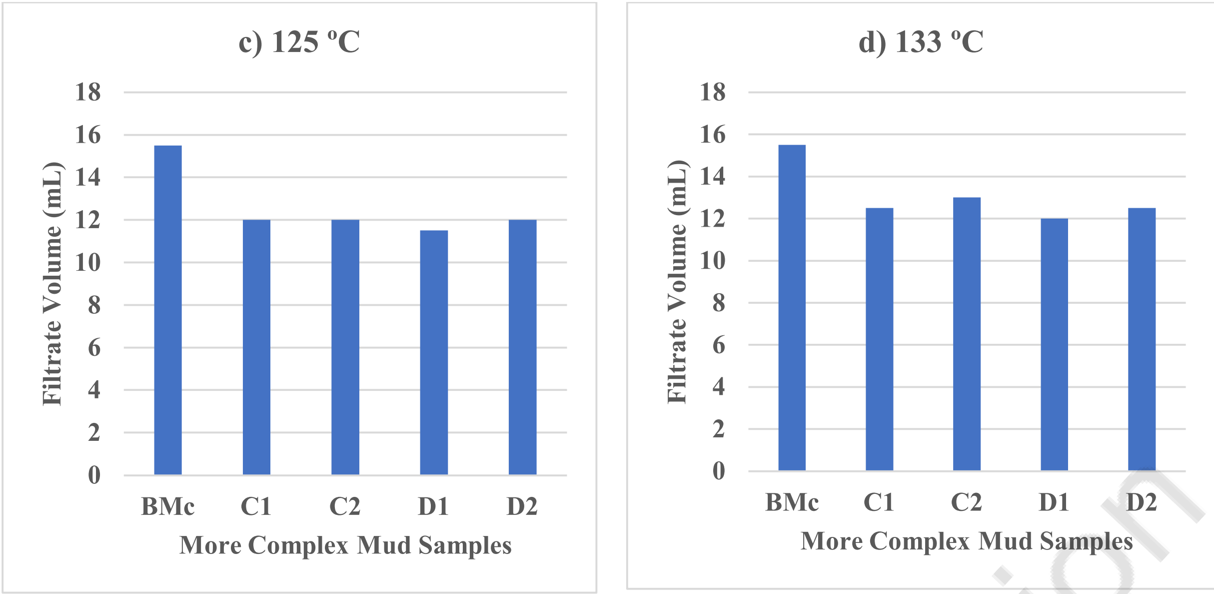


Figure 4: API filtration results after mud aging process at 75 °C, 100 °C, 125°C and 133°C for more complex water-based drilling mud

From the results of laboratory tests presented on this figure, it can be concluded that values of API filtration decreased for every mud sample with added mandarin peel powder in regard to base mud, and that this eco-friendly additive has positive effect on the filtration properties of the mud. It is also evident for muds which have concluded aging process up to 100 °C that there is no significant difference between muds to which 1% and 2% of mandarin peel powder was added, i.e. slightly better results were obtained with 2% of added mandarin peel powder.

This trend is identical as for basic water-based drilling mud with added mandarin peel powder. As for the differences in results between the two groups of different particle sizes, insignificant differences were recorded at the same concentration, which also matches the results for basic water-based drilling mud with added mandarin peel powder.

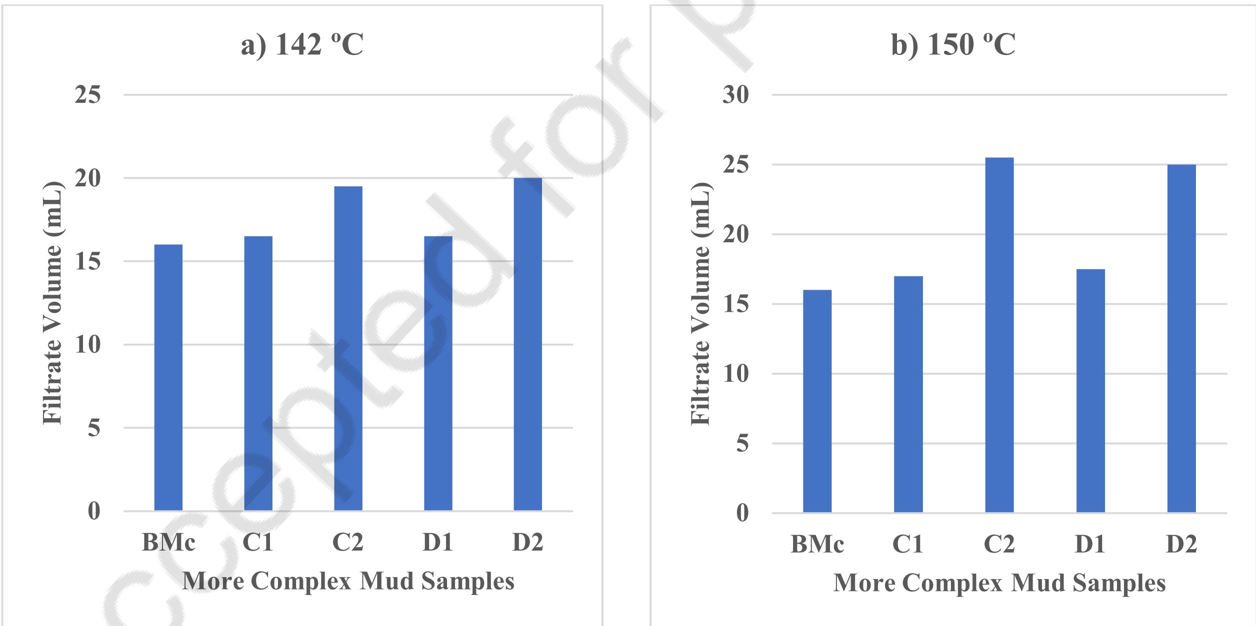


Figure 5: API filtration results after mud aging process at 142 °C and 150 °C for more complex water-based drilling mud

For higher temperatures of mud aging process (125 °C and 133 °C), API filtration also decreased for every mud sample with added mandarin peel powder in regard to base mud, so mandarin peel powder still kept its positive effect on the filtration properties of the mud. By raising the temperature of the mud aging process to 133 °C, positive influence of this additive on filtration is less pronounced than in the case of muds that have undergone the mud aging process up to a temperature of 100 °C. Presented results doesn't show significant difference in results between muds to which 1% and 2% of mandarin peel powder was added in mud samples that completed mud aging process at temperatures of 125 °C and 133 °C, and the same applies for differences in results between the two groups of different particle sizes.

Figure 5 shows the results of API filtration laboratory tests for the five mud samples after 16 hours hot roll mud aging at temperature of 142 °C and 150 °C. From the results presented on this figure, it can be seen that values of API filtration increased for every mud sample with added mandarin peel powder in regard to base mud, which indicates that at these temperatures the positive effect of this additive on the filtration properties of the mud was completely lost. After mud aging process on these temperatures, muds to which 1% of mandarin peel powder was added shows better results compared to muds in which 2% of mandarin peel powder was added but considering that filtration results are worse compared to base mud, these data are not so important. As well as for all previously shown sets of laboratory results, insignificant differences in results were observed between the two groups of different particle sizes, at the same concentration.

4. Discussion

All obtained results of laboratory research were compared for basic and more complex mud in order to more accurately determine the impact of mandarin peel powder after the mud aging process. The research carried out on the basic (bentonite-based) drilling mud provides a detailed insight into the effect of mandarin peel powder on the filtration properties of the mud subjected to the aging process from 75 °C to 150 °C temperature range. **Figure 6** shows all filtration results for this type of drilling mud, presented to indicate the impact of mandarin peel powder on basic mud, compared to base mud without this additive. This figure shows that the positive influence of mandarin peel powder is most significantly pronounced up to a temperature of 100 °C, while after that temperature this additive gradually loses its ability to reduce mud filtration. Temperature limit for positive effect on the filtration properties of basic drilling mud with added mandarin peel powder is 133 °C. Basic drilling mud with added mandarin peel powder that completed aging process on temperatures higher than 133 °C shows rapid decline of filtration control and complete loss of the positive influence that this additive provided at lower temperatures. Also, it can be noted that the filtration control is more pronounced up to a temperature of 125 °C, since a decrease in the volume of filtrate for muds containing mandarin peel powder is over 30% compared to the base mud.

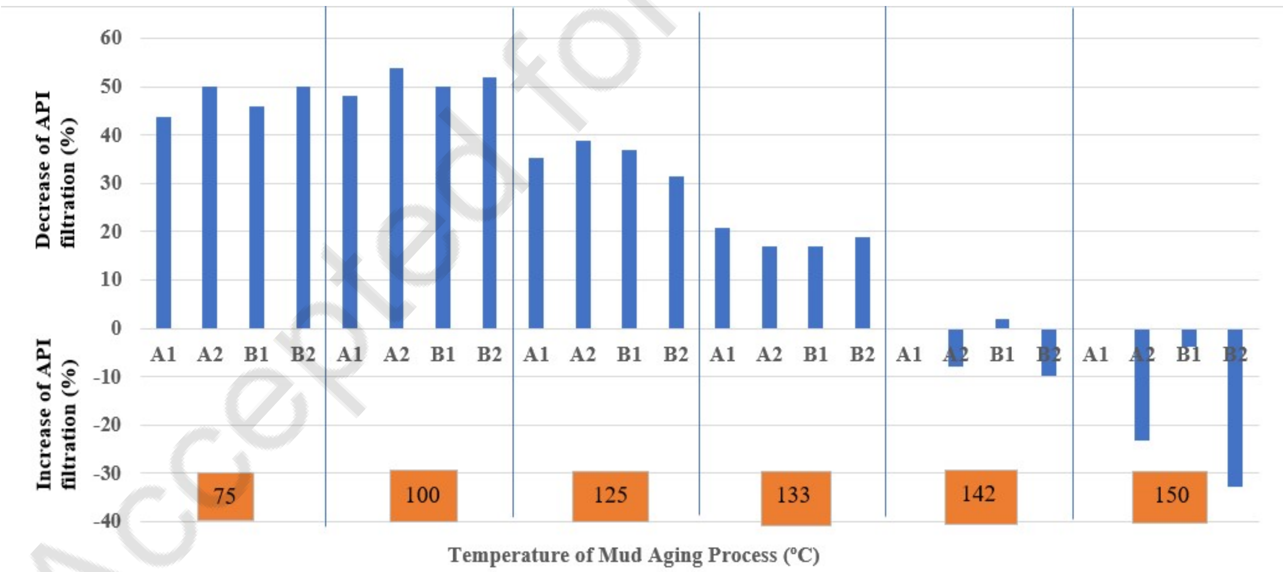


Figure 6: Effect of mandarin peel powder on API filtration in basic water-based drilling mud after mud aging process

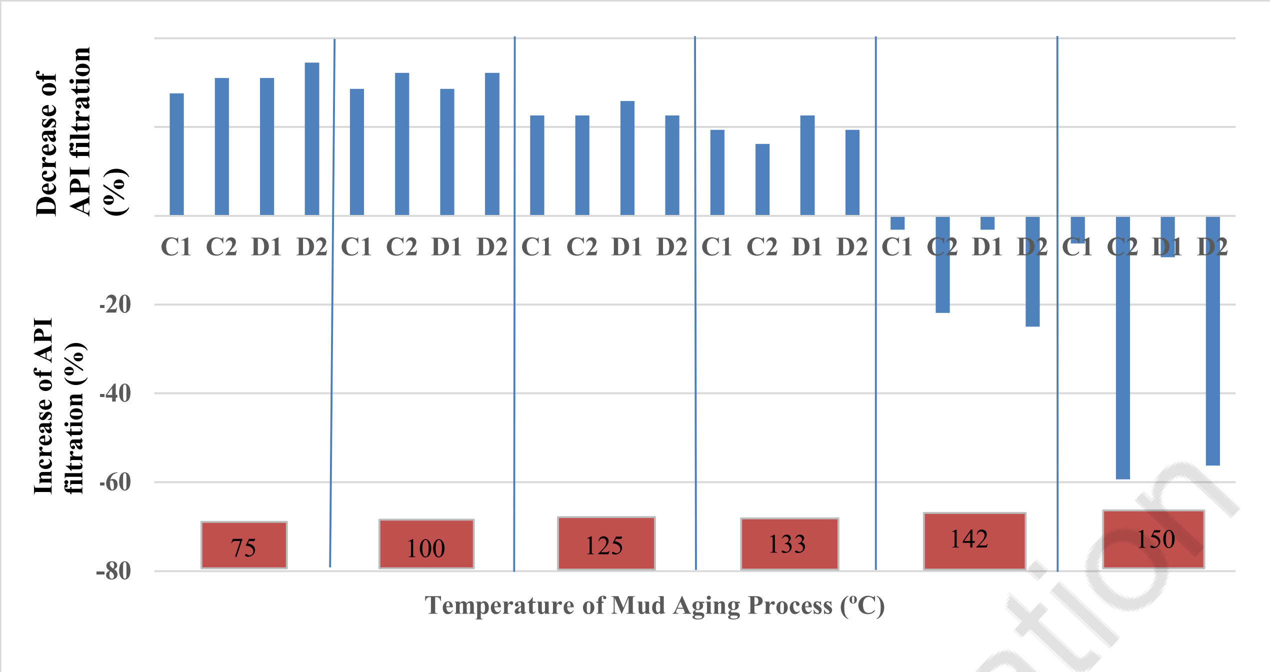


Figure 7: Effect of mandarin peel powder on API filtration in more complex water-based drilling mud after mud aging process

Figure 7 shows all filtration results for more complex composition of water-based drilling mud, presented to indicate the impact of mandarin peel powder in this type of mud, compared to base mud without this additive.

Since PAC R is component of the base mud, the positive influence of mandarin peel powder in this drilling mud composition is much more difficult to obtain compared to previous set of tests performed on basic (bentonite-based) mud. The influence of PAC R is best seen in **Table 3**, where it is shown how much the filtration of the more complex base mud has decreased, which contains this additive, compared to the basic base mud in which it is not included. Filtration of more complex base mud decreased from 37.3% to 46.2% compared to basic mud, when comparing the values for the entire temperature range of the mud aging process. These values show how difficult it is to achieve further reductions in filtration when PAC R is present in the base mud composition. Still, mandarin peel powder proved positive effect on the filtration property of more complex mud composition, and the trend is quite similar to results for basic mud. This figure shows that the positive influence of mandarin peel powder is maintained up to a temperature of 133 °C, so this temperature value can be defined as temperature limit for use of this eco-friendly organic additive. Like in previous case for basic mud, on temperatures higher than 133 °C this additive rapidly loses its ability to reduce drilling mud filtration.

Table 3: Comparison of basic and more complex base mud filtrate volume after 30 minutes of API filtration test

Temperature of mud aging process (°C)	Filtrate volume (mL)		Filtration decrease of more complex base mud related to basic base mud (%)
	Basic base mud	More complex base mud	
75	24	14,5	39.6
100	26	14	46.2
125	27	15.5	42.6
133	26.5	15.5	41.5
142	25.5	16	37.3
150	26	16	38.5

5. Conclusions

After conducting laboratory tests of API filtration on different samples of water-based drilling mud, it can be concluded that the positive influence of mandarin peel powder is present up to a temperature of 133 °C, at which the mud was heated during the mud aging process. This temperature limit, up to which the positive influence of this eco-friendly additive has been observed, applies on both basic mud and more complex mud. The positive influence of mandarin peel powder is most pronounced when the mud is subjected to an aging process up to a temperature of 100 °C, and in this case a filtration reduction of up to 53.9% was achieved in basic mud where 2% of mandarin peel powder (particles smaller than 0.1 mm) was added. For more complex mud samples that completed aging process up to a temperature of 100 °C, filtration reduction of up to 34.5% was achieved where 2% of mandarin peel powder (particles between 0.1 mm and 0.16 mm) was added. In the temperature range from 100 °C to 133 °C, the positive influence of this additive is still present, but it is becoming less pronounced. After aging of the mud at a temperature of 133 °C, the filtration reduction for the basic mud containing mandarin peel powder is in the range of 17.0% to 20.8%, which varies depending on the concentration and particle size of the added mandarin peel powder, and for the more complex mud, a decrease in filtrate volume from 16.1% to 22.6% was measured. It can be concluded that 133 °C is the temperature limit for the use of this additive, since at higher temperatures the influence of mandarin peel powder is completely lost. As was assumed considering the composition of the basic mud, mandarin peel powder significantly influenced the control of the filtration properties of the basic mud compared to the more complex mud up to a temperature of 125 °C, and at a temperature of 133 °C the results are quite similar for both mud compositions. Regarding the concentration of added mandarin peel powder in base mud, results are almost equal for both concentrations. Slightly better results were recorded when 2% of mandarin peel powder by volume of water was added to the mud compared to 1% by volume of water, after mud aging process up to 100 °C. For temperature range from 100 °C to 133 °C the results are quite similar for both concentrations. By comparing the filtration results of different particle sizes for the same concentration of added mandarin peel powder in the mud, it can be concluded that there is almost no difference due to this factor, which means that concentration of added mandarin peel powder is more important than different group of particle sizes.

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SAŽETAK

Utjecaj praha kore mandarine na filtracijska svojstva i temperaturnu stabilnost isplaka na bazi vode

Sve veća potražnja za energijom u svijetu, kao i trenutna geopolitička situacija, zahtijevaju od zemalja dodatna ulaganja u istraživanje i proizvodnju ugljikovodika iz vlastitih izvora. To znači da tvrtke moraju razviti nova polja koja su do sada ostala nerazrađena uglavnom zbog izuzetno zahtjevnih uvjeta u podzemlju gdje se ona nalaze (duboko more, visoka temperatura, visoki tlak, teška nafta, itd.). Razvoj ovih novih polja zahtijeva razvoj i usvajanje novih tehnologija, između ostalog, i razvoj temperaturno stabilnog bušotinskih fluida koji mogu ispuniti sve zadatke sukladno tehničkim izazovima koji se pred njih stavljaju. Osim tehnoloških izazova, raste i zabrinutost vezana uz utjecaj bušaćih operacija na okoliš. Sve navedeno potiče industriju na razvoj novih, cjenovno povoljnijih i ekološki prihvatljivih aditiva koji će moći zadovoljiti sve tehničko-tehnološke zahtjeve i izazove suvremenog bušenja. Posljednjih nekoliko godina sve je veći trend laboratorijskih istraživanja koja uključuju različite vrste biorazgradivog otpada kao potencijalnih aditiva kojima se u isplaci mogu postići korisna svojstva. U ovom radu ispituje se utjecaj praha kore mandarine na filtracijska svojstva isplake nakon procesa starenja pri povišenim temperaturama. Ovaj ekološki prihvatljivi aditiva dodavan je u isplake na bazi vode u koncentracijama od 1% i 2% na volumen vode. Ispitivanja su pokazala stabilna filtracijska svojstva isplake na bazi vode koja sadrži prah kore mandarine i nakon izlaganja isplake temperaturama višim od 130 °C.

Ključne riječi:
prah kore mandarine, isplaka, filtracija, starenje isplake

Author's contribution

This paper is a part of PhD research of the author **Igor Medved** (PhD student, graduate engineer of petroleum engineering) who initialized the idea, lead the laboratory research, participated in interpretation of the laboratory results, discussion and wrote the whole paper. The supervisor of PhD thesis, **Borivoje Pašić** (PhD, Associated Professor) provided the evaluation of the overall laboratory testing results and made a critical revision of the paper. **Petar Mijić** (PhD, Postdoctoral researcher) participated in the laboratory research and prepared one part of introduction section. All authors participated in writing conclusion of this paper.

3. DISCUSSION

In the first phase of laboratory research on the influence of mandarin peel on water-based drilling mud, API filtration of mud samples with added mandarin peel powder was performed. In order to obtain the best possible results that show the influence of mandarin peel on the filtration properties, bentonite suspension was selected as the base drilling mud. Results of filtration test obtained on this type of mud was compared with results obtained with eight combinations of drilling muds that had a different concentration of mandarin peel powder of different particle sizes in its composition. More precisely, four drilling muds contained mandarin peel powder with particles smaller than 0.10 mm (marked as A1, A2, A3 and A4), and other four drilling muds contained mandarin peel powder with particles sizes between 0.10 and 0.16 mm (marked as B1, B2, B3 and B4), that was added to mud in four different concentrations (0.5%, 1%, 1.5%, and 2% by volume of water). Data obtained by this type of laboratory tests showed that mandarin peel powder has significantly improved filtration properties of drilling mud and best results was achieved with water-based drilling mud (marked as B4) that had 2% of mandarin peel powder by volume of water, with 44,4% of filtrate volume reduction compared to base mud **(Medved et al., 2022a)**. The solubility of mandarin powder in water is about 28% **(Ojha et al., 2016)**; so it can be concluded that the viscosity of the filtrate increases what leads to increased resistance to leakage through a drilling mud cake or ceramic disc, and that results in a decrease of filtrate volume **(Medved et al., 2022a, Medved et al., 2022b)**. Considering the particle sizes, slightly better results were obtained for larger particles (muds B1, B2, B3 and B4), between 0.10 mm and 0.16 mm. However, for same concentration in the mud this group of particle size improved filtration properties only for 3,7% to 15,6% compared to drilling muds contained mandarin peel powder with particles smaller than 0.10 mm (marked as A1, A2, A3 and A4), so significant difference was not recorded. SEM (Scanning Electron Microscope) images taken on mud cake surface show no significant change in texture after filtration test was conducted on base mud. For mud samples that contained mandarin peel powder, larger accumulations can be seen over the entire surface. Logical assumption is that these are mandarin peel particles that are filling small pores in the created mud cake, resulting in a significant decrease in API filtration values **(Medved et al., 2022b)**.

Next phase of research (after performed tests in room conditions) included measurements on Permeability Plugging Tester at 88 °C and a differential pressure of 34.5 bar using ceramic discs with permeabilities of 0.4 μm^2 (400 mD) and 0.75 μm^2 (750 mD). For this type of research, the entire concentration range of mandarin peel powder was not included, only muds with 1% and 2% of mandarin peel powder in its composition (muds A2, A4, B2 and B4). Results showed that volume of filtrate was significantly reduced, and spurt loss is also significantly lower compared to the base mud, up to 75% for mud B4 (disc permeability of 0.75 μm^2). In order to study filtration properties in more detail for muds with added mandarin peel powder at elevated temperature and pressure, additional PPT filtration tests were conducted and the same compositions and mud marking system were used (shown in **Table 3-1**) as in previously published papers.

Table 3-1. Drilling mud composition for PPT filtration test

Drilling Mud Mark	Drilling Mud Composition			
	Bentonite (g/L)	NaOH (g/L)	Mandarin peel powder concentration (% by volume of water)	Mandarin peel powder particle size group (mm)
BM	60	1	-	-
A1	60	1	0.5	smaller than 0,10
A2	60	1	1	smaller than 0,10
A3	60	1	1.5	smaller than 0,10
A4	60	1	2.0	smaller than 0,10
B1	60	1	0.5	between 0,10 and 0,16
B2	60	1	1	between 0,10 and 0,16
B3	60	1	1.5	between 0,10 and 0,16
B4	60	1	2	between 0,10 and 0,16

Table 3-2 shows results for PPT filtration through the ceramic disc with permeability of 0.4 μm^2 (400 mD).

Table 3-2. PPT filtration results (ceramic disc with a permeability of 0.4 µm²)

Disc permeability	0.4 µm² (400 mD)								
Drilling mud	BM	A1	A2	A3	A4	B1	B2	B3	B4
Filtrate volume after 7,5 min, ml	15	14	9	8,5	7,5	12,5	9	8,5	7
Filtrate volume after 30 min, ml	26	24	17	15	13	22	16	15,5	12
PPT filtrate volume, ml	52	48	34	30	26	44	32	31	24
Spurt Loss, ml	8	8	2	4	4	6	4	3	4

All muds to which mandarin peel powder was added recorded a positive effect in terms of filtration properties, considering that the filtrate volume was reduced, as well as the spurt loss. Only a slight improvement is visible in drilling muds to which 0.5% mandarin peel powder was added, while at all other concentrations a significant improvement of this property is noticeable, with observation that increasing the concentration of this additive continues to improve mud filtration property. As in the case of API filtration results, slightly better results were obtained for particle sizes from 0.10 to 0.16 mm compared to particles smaller than 0.1 mm at the same concentration, but this difference between these two groups can be considered insignificant.

Table 3-3 shows results for PPT filtration through the ceramic disc with permeability of 0.75 µm² (750 mD).

Table 3-3. PPT filtration results (ceramic disc with a permeability of 0.75 µm²)

Disc permeability	0.75 µm² (750 mD)								
Drilling mud	BM	A1	A2	A3	A4	B1	B2	B3	B4
Filtrate volume after 7,5 min, ml	17	16	12,5	12	8	15,5	10,5	9,5	6
Filtrate volume after 30 min, ml	26	25	18,5	19,5	11	25	17,5	15,5	10
PPT filtrate volume, ml	52	50	37	39	22	50	35	31	20
Spurt Loss, ml	16	14	13	9	10	12	7	7	4

Similar to previous data, every drilling mud to which mandarin peel powder was added recorded a positive effect in the filtrate volume reduction and lowering value of the spurt loss. The drilling mud that has 1% or more mandarin peel powder in its composition, significantly improved the filtration property, with a note that better results were obtained for particle sizes from 0.10 to 0.16 mm. For PPT filtration through the ceramic disc with permeability of 0.75 μm^2 (750 mD) difference between these two groups of particle sizes are greater than through the ceramic disc with permeability of 0.4 μm^2 (400 mD). An explanation of why larger particles better fill the medium with higher permeability (better connectivity between the pores) is that permeability is related to the porosity, which means that the pores are also larger in volume, so smaller particles can more easily pass through the pores while larger ones fill it more effectively. This claim is also supported by the significant difference in the spurt loss between these two groups of different particle sizes. Also, it is important to note that different particle sizes within group are beneficial and make a positive contribute to the creation of internal bridging because they are more effectively distributed within the pores.

In the final phase of the water-based drilling mud filtration laboratory research, mud samples (marked as BM, A1, A2, B1, B2, BMc, C1, C2, D1 and D2) were conducted to hot-roll aging process with temperature range from 75 °C do 150 °C. For this type of laboratory measurements, drilling muds with a more complex composition (marked as BMc, C1, C2, D1 and D2) were prepared in order to examine if the positive properties of mandarin peel powder can further improve mud filtration properties on elevated temperatures. Although the mandarin peel powder significantly improves the filtration properties of mud with a basic composition, the positive effect of this eco-friendly material is also present in more complex mud composition. Filtrate volume reduced from 16,1% to 34,5% with added mandarin peel powder in different concentrations, although this mud composition already contains PAC R - an additive that improves the filtration properties of the mud. Also, with temperature increase a similar trend for filtration properties of more complex mud samples was observed as for basic mud samples (**Medved et al., 2023**).

While performing drilling operations through underground formations with high clay content, such as shale formation, contact with water phase from mud can cause hydration of the clay minerals and consequently change the rock volume due to cohesive strength reduction. The hydration of this type of the clay minerals during drilling operations can lead to more than a few problems and the main one is the swelling of formation, which creates a significant possibility for the occurrence of well instability. In order to successfully drill a wellbore, it is necessary to design a mud that doesn't cause physico-chemical interaction with the formation that can result with wellbore instability, and it should also have the small value of the filtrate volume that penetrates into the near-wellbore zone to form a thin and impermeable filter cake. Laboratory research to determine pellets swelling was made on Dynamic Linear Swell Meter, and first set of data was obtained at room temperature, while second phase of the laboratory research included measurements at 90 °C. As was the case with the filtration results, each mud sample with a certain concentration of mandarin peel powder showed a reduction of the pellet swelling. **Figure 3-1** is the most appropriate to show the pellet swelling reduction of eight mud samples with different mandarin peel powder concentrations in regard to the base mud.

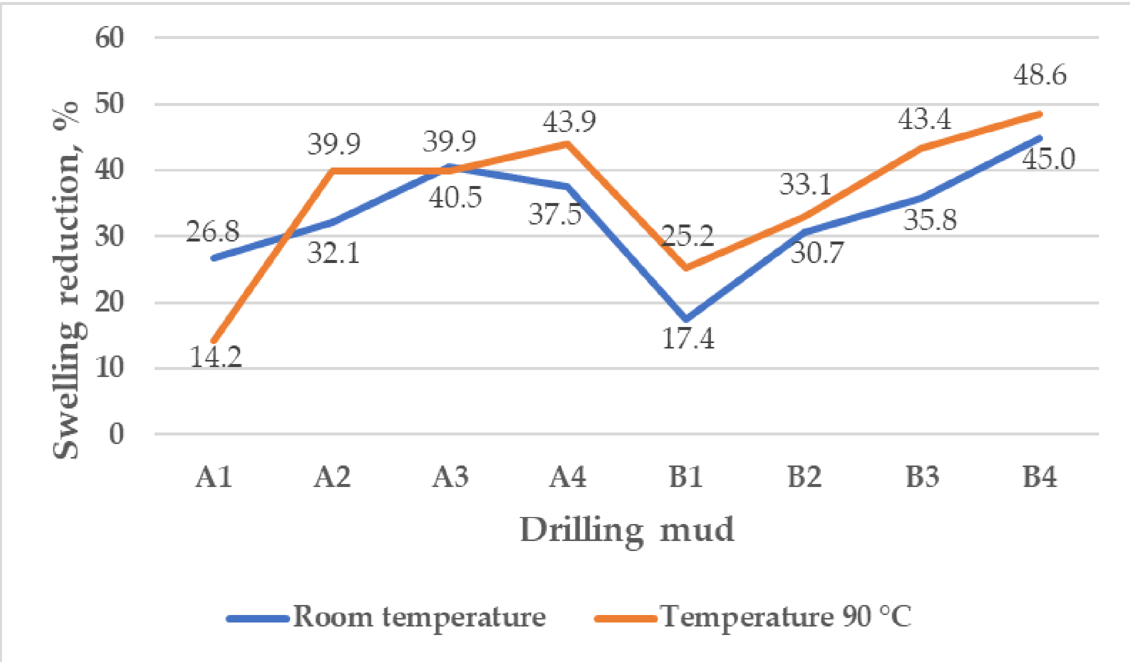

Figure 3-1. Pellet swelling reduction in different drilling muds with certain mandarin peel powder concentration compared to base mud after 24 h **(Medved et al., 2022b)**

Drilling mud with added mandarin peel powder of particle size from 0.10 mm to 0.16 mm shows same trend of swelling reduction at room temperature and at 90 °C, an increasingly pronounced positive effect as the concentration of this additive in the mud increases from 0.5% to 2% by volume of water. For particles smaller than 0.10 mm trend is not the same as for particles between 0.10 mm and 0.16 mm because there is no increased swelling reduction with increasing concentration of mandarin peel powder at room temperature (the best result is obtained with 1.5% of mandarin peel powder by volume of water). The most positive cognition of this part of research is that this additive has a positive effect on reducing swelling even at elevated temperatures, moreover the results are even better at 90 °C than at room temperature which confirms the positive influence of mandarin peel powder on the wellbore stability at elevated temperatures.

Rheological parameters (plastic viscosity, yield point and gels strength) were determined using a Fann viscometer 35A. After grinding the mandarin peel, it was sieved to obtain a powder in different groups of particle sizes: less than 0.10 mm and between 0.10 and 0.16 mm. The tests were carried out with identical concentrations as in the paper **Al Hameedi et al. (2020a)** but adding mandarin peel powder in a concentration higher than 2% by volume of water resulted in a significant increase in viscosity (mud samples gelled very quickly) and its value could no longer be measured. Results presented in this doctoral thesis are obtained up to mandarin peel concentration of 2 % by volume of water. The reason for such rapid gelation when more than 2% of mandarin peel powder is added to the base mud lies in the fact that there is a significant amount of pectin in the mandarin peel. Pectin is a carbohydrate found in fruits, and its concentration is particularly high in citrus fruit and it is a natural thickener and gelling agent. The exact concentration of pectin in the mandarin peel powder used in this laboratory research was measured on a VWR UV-1600 PC spectrophotometer (VWR, Pennsylvania, USA). The determination of total pectin content was carried out according to the International Federation of Fruit Juice Producers (IFU) protocol and after samples were prepared and filtered through Whatman No.40 filter paper, colorimetric determination was carried out on a spectrophotometer. Pectin content for mandarin peel powder with particles smaller than 0.10 mm is 81.43 mg per g of mandarin peel powder and for particles sizes between 0.10 mm and 0.16 mm pectin content is 65.53 mg per g of mandarin peel powder.

It was determined that by increasing the concentration of mandarin peel powder generally increases all the values of rheological properties (plastic viscosity, yield point and 10-s gel and 10-min gel strengths). By increasing the concentration of mandarin peel powder, plastic viscosity increased slightly up to a concentration of 1.5% by volume of water regardless of particle size. For drilling muds containing larger mandarin particles (between 0.1 and 0.16 mm), after increasing the mandarin peel powder concentration of 2% by volume of water a significant increase in plastic viscosity was obtained (129%) **(Medved et al., 2022a)**. Yield point values obtained at concentrations up to 1% by volume of water are similar to those in base mud, while at higher concentrations they follow the trend of plastic viscosity results. When comparing the influence of particle size on yield point values, it is shown that similar values were obtained at concentrations of 1.5 and 2% by volume of water, while at smaller concentration the values are slightly higher for muds with smaller particles. The gel strength values of mud containing smaller particles increase for concentrations up to 2% by volume of water (increase related to values obtained with base mud was 16%) and the similar trend was obtained for muds containing larger particles up to concentration of 1.5% by volume of water, after which it increases significantly (increase related to values obtained with base mud was 45 %) **(Medved et al., 2022a)**. Generally, by adding mandarin peel powder (both sizes) rheological parameters increase but remain within acceptable limits up to concentration of 1.5% by volume of water.

Considering that one of the main hypotheses of this doctoral thesis is that the toxicity of the water-based drilling mud would be reduced with added mandarin peel powder, ecotoxicity tests were also carried out using bacteria Vibrio fischeri. The method for determining aerobic toxicity is in accordance with the norm HRN/EN ISO 11348-1:2000 (Water quality – Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri, method using freshly prepared bacteria). The method is based on the assessment of the decrease in the physiological activity of bacteria Vibrio fischeri in the presence of toxic substances. The tested samples are categorized into the different categories of toxicity (**Table 3-4**), considering the toxic unit (TU) values, and this value depends on EC_{50}, which represents the effective concentration that causes a negative effect in 50% of the tested organisms.

Table 3-4. Sample categorization according to toxic unit (TU) value

Categorization according to toxic unit (TU) value
TU<0,4 = non-toxic
0,4<TU<1 = slightly toxic
1<TU<10 = toxic
10<TU<100 = highly toxic
TU>100 = extremely toxic

As part of this research, the toxicity of water-based drilling mud samples with commercially used additives was determined and compared with the base mud to which mandarin peel powder was added. Commercially used additives included in this research are modified starch used for filtration control, guar gum that is used to maintain rheological parametres and potassium chloride (KCl) used for maintaining the wellbore stability. All the listed additives were added in the recommended concentrations in order to achieve the listed properties, while a concentration of 1.5% by volume of water was chosen for the mandarin peel powder, considering that at this concentration material achieves the best results when all the listed properties are taken into account. **Table 3-5** shows results of samples tested for ecotoxicity. The EC_{50} value expressed as a percentage expresses the amount of sample required to cause a measured toxic effect per volume of tested organisms, meaning that the lower the EC_{50} value is, the sample is more toxic.

Table 3-5. Ecotoxicity of tested water-based drilling muds

Sample No.	EC_{50} (%)	TU (-)	Categorization according to TU value	Water-based drilling mud composition
Sample 1	60,65	1,65	toxic	bentonite 60 g/L; NaOH 1 g/L; mandarin peel powder 1.5% by volume of water
Sample 2	0,97	100,09	highly toxic	bentonite 60 g/L; NaOH 1 g/L; guar gum 0.8% by volume of water
Sample 3	3,76	26,60	highly toxic	bentonite 60 g/L; NaOH 1 g/L; modified starch 3.0% by volume of water
Sample 4	25,47	3,93	toxic	bentonite 60 g/L; NaOH 1 g/L; KCl 15.0% by volume of water

According to the obtained results, all tested samples are in the group of toxic to highly toxic per toxic unit value, but base mud with added mandarin peel powder has the lowest value and is close to slightly toxic category. The assumption was that the base mud with added potassium chloride would be the most toxic to the tested bacteria, however, the results showed otherwise. The reason for this may be that the Vibrio fischeri bacteria was isolated from a squid that lives in salt water and was adapted to conditions with a high concentration of chloride ions, and its sensitivity to KCl was low. If this additive were subjected to another test organism, this additive would most likely prove to be more toxic than other tested additives. This part of research shows that toxicity level of water-based drilling mud is reduced by using mandarin peel powder, compared to usually used commercial additives so progress has also been made in this field by using this material.

In order to determine the biodegradability of tested samples (to test whether the sample can be biologically processed), two chemical analyzes are performed: biochemical oxygen demand (BOD) and chemical oxygen demand (COD). If the BOD/COD ratio is equal to or greater than 0.5, it can be determined that the sample can be biologically processed because its biodegradability is equal to or greater than 50%. **Table 3-6** shows results of different water-based drilling muds tested for biodegradability.

Table 3-6. Biodegradability of tested water-based drilling muds

Sample No.	COD value (mgO_2/L)	BOD value (mgO_2/L)	BOD/COD ratio	Biodegradability (BOD/COD ≥ 0,5)	Water-based drilling mud composition
Sample 1	20980	11738	0.559	YES	bentonite 60 g/L; NaOH 1 g/L; mandarin peel powder 1.5% by volume of water
Sample 2	5954	4480	0.752	YES	bentonite 60 g/L; NaOH 1 g/L; guar gum 0.8% by volume of water
Sample 3	25706	16630	0.647	YES	bentonite 60 g/L; NaOH 1 g/L; modified starch 3.0% by volume of water
Sample 4	29 (total organic carbon)	-	-	NO	bentonite 60 g/L; NaOH 1 g/L; KCl 15.0% by volume of water

According to the obtained results, it is evident that all tested muds are biodegradable, except for the one to which potassium chloride (KCl) was added. This mud is not biodegradable because it contains all inorganic components. For this sample, the presence of organic matter, i.e. total organic carbon, was measured instead of chemical oxygen demand since chloride ions interfere with the determination of this value. Regarding the biochemical oxygen demand value determination, the oxygen concentration at the beginning of laboratory test and after five days was the same, indicating that the microorganisms did not consume oxygen because there was no organic matter present. It is evident from the presented results that the mud which contains mandarin peel powder in its composition is biodegradable and there are no obstacles to its use according to this parameter.

4. CONCLUSION

In recent years, scientists and industry have devoted a lot of attention to research the possibilities of using waste for various useful purposes, and one of the types of waste that is in the focus of various research groups is biodegradable waste. Different types of biodegradable waste have been tested with more or less success, and previous research published on this topic suggested that mandarin peel could have the necessary properties to positively affect on filtration and rheological properties of the drilling mud as well as reduction of the swelling of the clay minerals in the rock and enhancing wellbore stability. There are not many such studies, and the currently published results leave doubts about the potential application of this type of biodegradable waste as an additive that could be applied in field conditions. The main shortcomings of the previously published set of results are mainly related to the conditions in which the laboratory measurements were carried out (only in room conditions), and that there is no data about the impact on the wellbore stability. Also, in the preparation of this type of waste for use in water-based drilling mud, after the drying phase and removal of moisture from the mandarin peel, the final phase was grinding, without sieving. Such a preparation of mandarin peel does not give successful results when conducting various tests on mud samples to which this additive was added in different concentration but with unknown particles size. Within this doctoral dissertation, laboratory tests were conducted to determine influence of mandarin peel concentration and particle size on important mud properties: filtration, rheological properties, and the influence on the swelling of laboratory prepared artificial rock samples (pellets).

On the basis of the conducted laboratory tests and the analysis of the results, useful insights were obtained on the effect of mandarin peel on the observed mud properties. Results show that mandarin peel have positive effect on mud filtration, since every mud sample with added mandarin peel powder showed decrease of filtrate volume. The selected concentrations of mandarin peel powder were from 0.5% to 2% by volume of water, and by increasing concentration of this material, the API filtration continuously decreases. Reduction of filtrate volume was up to 44% in room conditions, and even better results were recorded in conditions of elevated temperature and pressure on PPT device (filtrate reduction up to 61,5%). Mud samples with 2% of added mandarin peel powder obtained best results on these laboratory tests, but significant improvements were already observed in samples with 1% of mandarin peel powder by volume of water. A valuable insight related to the filtration properties of mud is that mandarin peel manages to further improve this parameter even with the presence of commercial additives used for these purposes in mud composition, such as PAC R. Also, one group of laboratory tests was carried out to prove the temperature stability of the drilling mud containing mandarin peel powder up to 133 °C, through the hot roll aging process. Positive influence of mandarin peel on API filtration is most significantly pronounced up to a temperature of 100 °C and there is no increase of the filtration volume with increasing temperature up to mentioned temperature limit of 133 °C. For this entire set of laboratory research, it can be concluded that particles with a size between 0.10 mm and 0.16 mm have a slightly better effect on filtration properties compared to particles smaller than 0.10 mm, but no significant difference in the obtained results was observed between these two groups.

An exceptionally positive influence of mandarin peel powder was also observed in data obtained after swelling of pellets that have a water sensible clay component in their composition. Reduction of pellet swelling in muds containing mandarin peel, compared to the base mud, was already pronounces after adding 0.5% of this additive by volume of water. However, the best results were recorded with muds containing 2% of mandarin peel powder by volume of water and reduction in pellet swelling after 24 hours test was up to 45% in room conditions and up to 48.6% at 90 °C. Again, even better results were recorded in conditions of elevated temperature compared to room conditions and particles size between 0.10 mm and 0.16 mm have a slightly better effect on the pellet swelling reduction, so these results correlate well with results of filtration measurements which is essential to prove the improvement of the wellbore stability.

The rheological properties increase and remain within acceptable limits up to concentration of 1,5% by volume of water, when mandarin peel powder (both group of particle sizes) is added in water-based drilling mud. At a concentration of 2% by volume of water of mandarin peel powder (particles between 0,10 mm and 0,16 mm), rheological parameters significantly increase, resulting in increased pressure loss so, in general, it can be concluded that the optimal concentration of mandarin peel powder is up to 1.5% by volume of water for both tested particle sizes, although smaller particles could also be used at a slightly higher concentration.

By comparing the results on the observed mud properties of different particle sizes of mandarin peel powder, it can be concluded that slightly better results were obtained with larger particles between 0.10 mm and 0.16 mm but both sizes provide water-based drilling fluid with satisfactory properties. The recommended concentration of this material should be kept in the range of 1.0% to 1.5% due to greater negative deviations from the allowable limits obtained from tests of rheological properties on drilling muds that had 2% of mandarin peel by volume of water in their composition. In concentration range of 1.0% to 1.5% excellent results were obtained related to the filtration properties and wellbore stability so this concentration range can be considered optimal to meet all the necessary water-based mud properties.

Compared to previous tests in this field of research, a significant scientific contribution has been made in the field of drilling mud filtration properties, considering that research was conducted at elevated temperature and at elevated pressure. Also, the influence of mandarin peel powder on the wellbore stability by conducting swelling tests on artificial rock samples (pellets) has not been investigated so far and represents the most significant progress compared to previous research. In terms of rheological properties, there was not positive influence, but the results are not different compared to base drilling mud so this property does not eliminate the positive influence determined for filtration and wellbore stability. The need for sieving mandarin peel powder after grinding was also determined, since poor results are obtained if sieving is not included in this procedure, which was especially pronounced in the results of rheological properties.

Ecotoxicity measurements showed that toxicity of water-based drilling mud that has mandarin peel powder in its composition is reduced, compared to conventionally used commercial additives. This test confirmed the ecological component of using this type of material, and whole research confirmed the applicability of the circular economy concept in drilling technology. Considering the annual production of mandarin in Croatia, if its peel would be used for these purposes, according to the recommended concentration that would be added to the mud, amount of this additive would be enough for drilling significantly larger number of wells compared to current requirements of the domestic industry.

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6. BIOGRAPHY OF THE AUTHOR

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