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The Prospects and Challenges of Biopolymers for Enhanced Oil Recovery (EOR)

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ABSTRACT. Currently, Enhanced Oil Recovery (EOR) technology is being interested in the Indonesian state as an advanced technology that can recover oil remaining in the reservoir. The discovery of new resources and EOR efforts are predicted to result in increased oil production. This paper provides a review of main types of EOR methods, which are gas injection, thermal injection, and chemical injection; mechanism of polymer flooding; and biopolymer materials for EOR. Attention were given to xanthan gum, cellulose, guar gum, and lignin. Polymer flooding is a low-cost chemical injection method with a high rate of success. Polymer flooding has several advantages, including improving oil recovery by minimizing residual oil saturation, decreasing water output from oil well, and requiring less water compared with water flooding. Since the use of polymer flooding in the EOR activities, there is a lot of potential that biopolymers are materials that play a significant role in the application of EOR technology, because environmentally friendly properties and have advantages over synthetic polymers. Biopolymer can be modified to nano materials or grafted with synthetic polymer to improve its properties and stability. The modified biopolymers effectively increase the efficiency of biopolymers for EOR under the reservoir conditions. Native biopolymer recovered additional oil from 27 until 62% . Meanwhile, modification of biopolymer increased additional oil recovery up to 71%. The use of modified biopolymers can make the EOR process greener and more facile.

1. INTRODUCTION

The national demand for oil and natural gas energy remains high, but Indonesia's oil production was projected to continue to decline. Despite controlling fuel consumption and diversifying fuels with other fuels, the demand for fuel continued to increase each year. Domestic demand for crude oil was supplied in part by domestic production and in part by imports. Crude oil was subsequently refined into fuel and other important (non-fuel) petroleum products at refineries. In addition, fuel was utilized to power plants and other sectors, such as industry, transportation, household, commercial, and other sectors. Increased refinery capacity has an impact on increasing import crude oil. To meet the needs in each sector and power plant until 2050, it is necessary to provide oil of 146.6 million tonne of oil equivalent (MTOE), that value increased almost 3 times from the oil supply in 2018. Petroleum production is projected to decline at a rate of 3% per year to 13 MTOE by 2050. Oil production is not enough to meet the refinery's demand of 157 MTOE by 2050, so crude oil imports will be required to reach 146 MTOE by 2050 [1,2].

The decrease of oil production has many factors, including decreases oil and gas exploration activities and low levels of exploration success by oil and companies, a disadvantageous oil and gas investment environment for companies, and a lack of optimal application of Enhanced Oil Recovery (EOR) technology. Some optimization strategies for drilling development wells to increase oil production to maintain production levels in existing fields, accelerating the transition from resources to production, improve EOR for old fields, and implementing exploration strategies [3]. In Figure 1, it is expected that applying the EOR method can increase oil production in Indonesia.

In this study reported here, we investigate the main types of EOR methods, which are gas injection, thermal injection, and chemical injection. Chemical injection show that have more advantages than other methods, the most important substance in this method is polymers. A commonly used polymer in EOR activities is synthetic polymer, there are some challenges and have negative impact to environment of using synthetic polymer in EOR activities. So recently used biopolymer that have potential to EOR activities and mechanism of polymer flooding will be discussed.

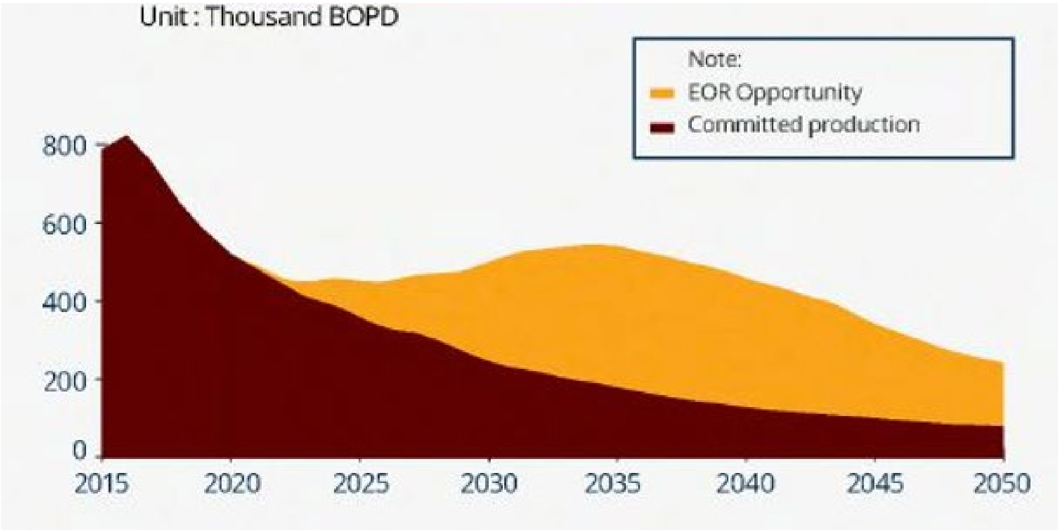


Figure 1. EOR Projection to Boost Production [1]

2. ENHANCED OIL RECOVERY

There are three primary stages of production in conventional oil fields. Oil from the reservoir naturally flows into the well in the early stages, but as the extraction of oil progresses, the pressure in the reservoir decreases and the flow of oil into the well decreases. As a result, secondary recovery is used to improve oil production. Injecting fluid into the well to enhance pressure and flow rate is known as secondary recovery [4]. The most commonly injected fluid is water. The flow of primary and secondary recovery methods, on the other hand, still leaves around 60%–70% of oil contained in reservoirs [5]. As a result, additional recovery may be implemented. Tertiary recovery, also known as enhanced oil recovery (EOR), is a method of extracting oil by energy from outside the reservoir. The energy obtained from the injection of particular fluids that interact with the oil to modify its density or viscosity, decrease rock-to-oil adhesives ("wettability") or connects high permeability flow routes in the reservoir. Particular fluids injected to reservoir also for modify the characteristics of the oil or rock in the reservoir, or change flow patterns within the reservoir to make oil flow into wells easier and improve oil acquisition (production) [6,7].

There are several main types of EOR methods including gas injection, chemical injection, and thermal injection. Gas injection typically uses CO_2, N_2, or natural gas to push oil in immiscible or miscible conditions. The gas injection mechanism consists of injecting gas into the subsurface. In the process of miscible gas, the gas mixes with or dissolves with the oil to increase its mobility and susceptibility to being driven by water. In the immiscible process, the gas does not dissolve in the oil but instead encourages the remaining oil, this method is often combined with water injection. The gas injection has a higher displacement efficiency than water flooding and may be used in a wider range of reservoirs, including limited permeability and heavy oil reservoirs [8].

Thermal injection is performed by injecting the heat into the subsurface, especially to recover hydrocarbons from heavy oil reservoirs. The thermal injection mechanism is a continuous stream of steam that is injected to pushes the oil into the production well, then the steam dissolves into the oil and reducing the viscosity of oil, making it easier for the oil to flow to the production well. Another thermal method is in-situ combustion by injecting air into the reservoir to reduce the viscosity of the oil and increase energy to move the oil by oxidizing a small portion of hydrocarbons to produce heat and gas. The combustion method has high risk but great opportunity to improve the recovery of heavy oil [4].

Chemical injection is by injecting chemicals to improve the efficiency of sweeps or fluid displacement performance. Commonly used chemicals consist of alkali, surfactants, and polymers. Chemical injection may be performed by using combinations of alkali-polymers, surfactant-polymers, or alkali-surfactant-polymers. The mechanism of chemical injection is constructed by adding insoluble polymers and/or surfactants to the water injected into the reservoir. Polymer or surfactant that is filled by water have higher viscosity than water so it can push more oil out of the reservoir [5,6].

The advantages and challenges of the main types of enhanced oil recovery methods are summarized in Table 1.

Table 1. The advantages and challenges of enhanced oil recovery methods

EOR Method	Advantages	Challenges	Ref.
Gas Injection	1. Using non-toxic and non-combustible materials 2. Without further effort, the location may be used for future injection for permanent CO_2 seques-tration once the project is completed.	1. Difficult to achieve Minimum Miscible Pressure (MMP) since the average MMP of oilfields in Indonesia are quite high 2. Lack of CO_2 transportation and surface facilities 3. Most of the existing wells in Indonesia are old wells that need to be rejuvenated before injection 4. High cost, because need separation unit, injection unit, tubing and pipeline should be anti-corrosive, and high CO_2 price 5. Social and environmental issues	[7,8]
Thermal Injection	6. Efficient for wells with high viscosity oil content and wells with low depths.	1. Steam injection methods are less efficient and economical when used in deep wells, thin and have low permeability. 2. Heat loss can occur through transmission and distribution pipelines	[9]
Chemical injection	1. Chemicals can reach low-permeability carbonate reservoirs that have been performed water injection and gas injection but still have high oil saturation remaining and are trapped in rocks. 2. Using non-toxic and non- cohasrrosive materials 3. The technology is almost the same as water flooding, so the method is simple 4. Less cost	1. Difficult to find the optimal chemical formulation taking into account emulsification capabilities, chemical retention, and adsorption loss on rock surfaces	[10]

Up to the 2000s, chemical injection methods were not as common as thermal and gas injection, but now chemical injection is starting to develop in the presence of large-scale projects ranging from laboratory work to field trials. Each chemical have a different function and the most important substance in this method is polymers [11].

Polymer flooding is a very mature method which has been used for over 40 years. It has been successfully implemented in many oilfields around the world. Fields testing have shown that polymer flooding can increasing crude oil recovery by 5-30% of original oil in place (OOIP) and further improve the oil recovery by 3% after water flooding is exhausted. Because of the decline in water output and improvement in oil production, the overall cost of polymer flooding is lower than water flooding. The method has an efficiency range of 0.7 to 1.75 lb polymers per bbl of additional oil output [12,13]

A commonly used synthetic polymer in the EOR method is hydrolyzed polyacrylamide (HPAM). HPAM has several advantages including its large availability, low manufacturing cost, and flexible features. However, the use of HPAM is very sensitive to reservoir conditions (temperature, salinity, shear, etc.) and have negative impacts on the environment due to the toxicity and carcinogenicity of residual monomers of these polymers [11,14]. From these problems, biopolymers become an interesting solution for the development of EOR method. Biopolymers have advantages such as cheap, easy to get, have biocompatible and biodegradable properties (environmentally friendly), and superior chemical stability [15].

3. RECENTLY USED BIOPOLYMER

3.1 Xanthan Gum

Xanthan gum is a polysaccharide biopolymer. It is produced by Xanthomonas campestris microbes on the carbohydrate media substrate, with protein supplements and inorganic nitrogen sources [11]. Xanthan gum have rigid polysaccharide chains, making it less sensitive to mechanical shear, high salinity, and varying ionic concentrations. Xanthan gum also has good resistance to high temperatures [12,16]. Where the polymer solution of commercial xanthan gum has a relatively constant viscosity at a temperature of 80ºC for more than 2 years. The viscosity of xanthan gum is not detected at above 100°C. Xanthan gum solution shows that their viscosity do not decrease at high shear pressure. However, there are some disadvantages of xanthan gum, namely its susceptibility to bacterial degradation. Where salinity-tolerant and anaerobic-aerobic microorganisms can degrade the xanthan gum chain causing loss of viscosity of the solution [17].

Xanthan gum polymer solutions recovered 8.8, 20.9, and 27.8 % additional oil after waterflood and cumulative oil recovered 32.8, 33.7, and 56.2 % when about 2.5, 3.8, and 3.9 cc pore volume of the polymer solutions injected using concentrations 1000, 4000 and 6000 ppm, respectively. The experiments were conducted under the core flooding test at laboratory deduction (30ºC, no salinity) [18].

There have been several modification efforts of xanthan gum to improve its physicochemical properties and enlarge its application. Several studies report that modified xanthan gum with TiO_2 nanoparticles to produced polymers as nano-polymer suspensions [19]; modified xanthan gum with chloride-substituted octyl phenoxy polyoxyethylene [20]; and modified xanthan gum with silica (SiO_2), rice husk ask (RHA) and acacia gum (AG) to produce polymers [21]. Modification of xanthan gum have purposed to improve its properties under conditions of high temperature and high salinity in the presence of oil phase. The results of the formulation showed lower interfacial tension in addition to higher viscosity effect compared to the using of xanthan gum alone. Therefore, the modification of xanthan gum is expected to apply to polymer flooding. Under reservoir conditions, xanthan gum modified with amide- and alkyl- nanosilicas recovered approximately 70.5% more OOIP [22].

3.2 Cellulose

Cellulose is a polysaccharide in which several D-glucose units are bound together. Cellulose and its derivatives are one of the most abundant sources of renewable biopolymer on earth [23] with annual production estimated at about 10 bn tonnes [24]. Cellulose is obtained from plants and wood. It is also synthesized by algae, tunics and bacteria [25]. Cellulose based products used in the process of exploration and exploitation of petroleum are carboxymethyl cellulose (CMC) and polyanionic cellulose (PAC) [26]. The disadvantage of cellulose is the nature of degradation that is a serious focus. The typical temperature limit for cellulose is from 135 to 149ºC. In addition to thermal degradation, oxidative decomposition can also occur [14].

Some conditions in oil wells such as high temperatures (>100ºC) and long retention times. Therefore, there is a need to increase the stability of cellulose by converting it to nanocellulose [27]. The synthesis of nanocellulose by grafting AMPS (2-acrylamide-2-methylpropane sulfonic acid) and hydrophobic groups (HG) was performed on nanocellulose [28] to improve the physical, mechanical, and chemical properties of nanocellulose the right choice for applications in the oil and gas industry especially offshore, deep water, extreme environmental drilling. Cellulose nanofibrils (CNF) also have the potential as injectable additives for enhanced oil recovery (EOR) [29]. The result of production through simultaneous grafting of N, N-Dimethylacrylamide (DMA) and Butyl Acrylate (BA) on CNF surfaces based on the ceric ammonium nitrate as an initiator to generate free radical polymerization. The result of cellulose modifications have higher salinity and temperature resistance than only cellulose, so it is potential to be applicable for polymer flooding [30].

Core flooding experiments revealed that fusion nanofluid was formulated by combining cellulose nanocrystal (CNC) and asymmetrically modified Janus graphene oxide attained additional oil recoveries of 22.96% and 12.24% from Berea and Edwards White, respectively. CNC recovered additional 18.62% and 9.80%, from Berea and Edwards White, respectively [31]. A Novel surface-functionalized cellulose nanocrystals were successfully prepared by hydrochloric acid hydrolysis and sulfonated modification. The modified cellulose can effectively enhance the oil recovery by 20.2% of OOIP with the permeability of $30.13x10^{-3}$ µm2 and reduce the oil water dynamic interfacial tension (IFT) down to 0.03 mN/m [32]. The use of modified cellulose can make the EOR process greener and more facile.

3.3 Guar Gum

Guar Gum is a biopolymer derived from the two annual endosperm leguminous plants Cyanaposis teragonalobus and Cyanaposis psoraloides and have hydrophilic and biodegradable properties [33]. Guar gum consists of a linear backbone chain unit (1-4)-β-D-mannopyranosyl with a branch point of α-D-galactopyranosyl unit attached by (1 – 6) linkages [34].

Guar gum is carbohydrate with long chain and the molecule weight about 1 – 2 MDa. Guar gum may be soluble in hot and cold water, but insoluble in nonpolar organic solvents. However, because guar gum is not sufficiently hydrated, the use of guar gum as EOR based fluid presents a potential risk of porous media plugging [35]. The advantages of guar gum are compatibility of various pH values and salinity. The viscosity of guar gum solution increases with increasing salinity concentration, but the salinity resistance of guar gum decreases with the increasing of divalent cations and may precipitate in high concentrations of calcium ions solution [36]. Guar gum has poor thermal stability and some molecules are insoluble at low temperature, so the viscosity of guar gum solutions increases with decreasing temperature.

Guar gum polymer solutions recovered cumulative oil 41.8, 57.1, and 61.2 % were injected for concentrations 1000, 4000 and 6000 ppm, respectively. The experiments were conducted under the core flooding test at laboratory deduction (30^{o}C, no salinity) [18]. Core displacement study showed that guar gum solution recovered the maximum additional oil of 27.13 % [37].

Modification of guar gum with nanoparticles may improve its rheological properties and chemical slugs stability for polymer flooding applications. A modified guar gum mixed with silica nanoparticles improves the effectiveness of guar gum by restoring 44.3% of the original oil in place [37].

3.4 Lignin

Lignin is one of the most aromatic natural complex polymers, along with cellulose and hemicellulose. Lignin is an amorphous polymer that is widely extracted as a byproduct in the pulping, papermaking, and agricultural industries [43–45]. The chemical structure of lignin varies depending on the kind of biomass and the extraction technique. Although lignin is insoluble in water, its hydrophobicity allows it to be soluble in inorganic solvents. The rheological characteristics of lignin are changed by concentration, according to rheological experiments. The dispersions form pseudoplastic fluids with shear-thinning tendencies as concentration increases. This is probably because the coagulation contacts between the aggregates of lignin particles and are disrupted as the shear rate increases [38,39].

There are several studies of lignin modifications to improve its rheological properties. Lignin modification to make micro and nano structure using low-sulfonate Kraft lignin (LSL)/polyvinylpyrrolidone (PVP) solutions in N, N-dimethylformamide (DMF) [40]. Lignin nanoparticles were homogeneously dispersed in the poly(3-hydroxybutyrate) (PHB) [41]. Composite solutions of polyacrylonitrile (PAN) with annual plant lignin (APL), PAN/APL. Lignin modifications show lower yield stresses, lower relaxation time, and lower viscosities than only lignin solution according to the dynamic frequency sweep measurements from -7^{o}C to 56^{o}C [42].

Table 2. The advantages and disadvantages of biopolymer application [14]

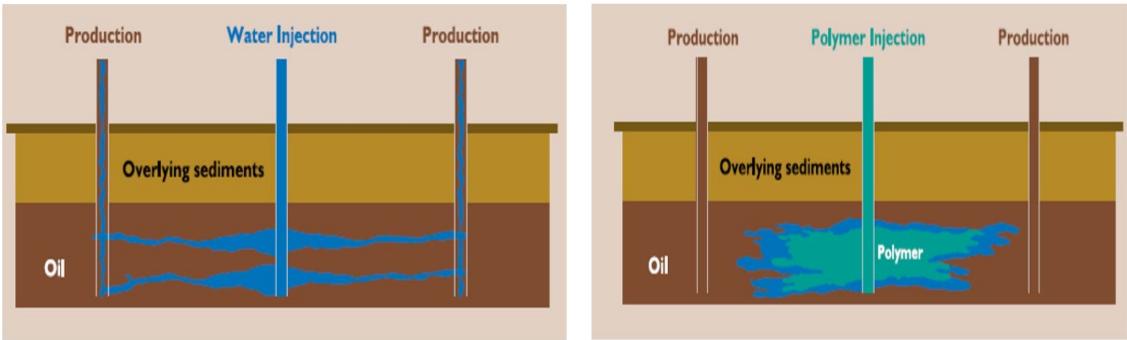
Biopolymer	Characteristic	Advantages	Disadvantages
Xanthan Gum	Soluble in hot and cold water, but insoluble in nonpolar organic solvents	1. Shear, salinity, and temperature resistance 2. Long term stability 3. Eco-friendly material	1. Potential plugging 2. Biodegradation and oxidation
Cellulose	Insoluble in water and organic solvents	1. Shear and temperature resistance 2. Eco-friendly material	1. Insolubility and hetero-geneous swelling 2. Biodegradation and oxidation
Guar Gum	Soluble in hot and cold water, but insoluble in nonpolar organic solvents	1. Good hydration properties 2. Wide range of pH and salinity resistance 3. Eco-friendly material	1. Plugging in porous media 2. Limited thermal stability 3. Lack of flexibility 4. Biodegradation and oxidation
Lignin	Insoluble in water, but soluble in organic solvents	1. Lower cost and large availability 2. Eco-friendly material	1. Insoluble in water 2. Oxidation and biodegradation

Lignin has been useful for several decades and has a reliable supply, but it has not been EOR pilot-tested because of various technological difficulties. Surfactants and foaming agents made from lignin have, nevertheless, been frequently employed in oil recovery. For example, in Indonesia, a collaborative effort has been made to adapt lignin-based surfactant technology to an oil field [20].

4. MECHANISM OF POLYMER FLOODING

Polymers, particularly hydrogel polymer, are materials that play an essential role in the application of EOR technology. Synthetic and biopolymer are two primary types of polymer used in conventional polymer flooding. One of the most common synthetic polymers is hydrolyzed polyacrylamide (HPAM), while xanthan gum is one of the most common biopolymers for the application of polymer flooding. When the polymer is injected into the water, it affected to rheological properties of the water [10].

Polymer flooding is used to increase stroke efficiency by increasing the mobility of injected fluids. Fingering phenomena will occur when only injecting water into the heterogeneous reservoir, and the injected fluid flows considerably easier than oil through the permeable medium due to its high permeability layer. Figure 2 depicts a comparison of fingering phenomena caused by water flooding and polymer flooding. At the end of this process, injected only water into the reservoir make the large reservoir area are not contacted by water [44].



(a) (b)

Figure 2. Comparison Fingering effect between Water Flooding (a) and Polymer Flooding (b) [43]

In typical polymer flooding projects, a polymer mixture is injected over a long period of time until nearly 1/3-1/2 of the reservoir pore volume is absorbed. The water then continuously injects the polymer "slug" to push the polymer slag and the oil fields in the front of it into the production well. Polymers were continuously injected for several years to achieve the desired pore volume. Adding polymers to the reservoir increases the viscosity of the water and decreases the relative permeability of the water, increasing the oil gain owing to higher fractional flow. The viscosity of polymer solutions is an important rheological characteristic. Polymer solutions have a higher viscosity than water, which helps sweep the oil through porous medium and improve oil recovery. The viscosity of the polymer slug may be improved in polymer flooding activities by using the following methods: raising the concentration of polymers in brine, decreasing salinity solvents, and using polymers with a high mlecular weight [11].

Table 3. Screening criteria of polymer flooding

Factor	Criteria of Polymer Flooding
Oil viscocity [cP]	<10000
Residual oil saturation [%]	>30
Formation salinity [ppm]	<250000
Temperature [F]	<250
Thickness [ft]	>10
Porosity [%]	>10
Permeability [mD]	>10

The high expense of delivering high concentrations, as well as injection issues such as high pressure during injection into drill wells, were both caused by the increase in polymer concentration. As a result, increasing the concentration of polymers to produce higher viscosity is not always a reasonable strategy in some cases. In contrast to high concentration polymers, high molecular weight polymers can create higher viscosity at lower polymer concentrations. As a result, using high molecular weight polymers to achieve higher viscosity at low concentrations might be beneficial. [45]. Polymers with a higher molecular weight might cause additional issues. Because the polymer molecule size might be larger than the pore size when the molecular weight is increased, this can produce injective difficulties or an increase in inaccessible pore volume (IPV). The volume of pore space inaccessible to polymers is called IPV. When the particle size is larger than the pore size, polymer molecules cannot pass through. There are several more drawbacks of polymer flooding, as shown in Table 3 [46].

5. CONCLUSION

The EOR method is feasible to significantly increase oil recovery from oil reservoirs that have been produced by the primary method. There are three main types of EOR methods: gas injection, chemical injection, and thermal injection. The significant greenhouse gas footprint, limited heavy oil/bitumen recovery, and difficulty in stopping operations in emergency conditions are only a few of the disadvantages. There is a potential for a better method of recovering residuals oil following water injection. Chemical injection is one of the strategies that might be used. Surfactants, alkali, and polymers are three primary substances injected. Polymer flooding is a low-cost chemical EOR method with a high rate of success. Fields testing have shown that polymer flooding can increasing crude oil recovery by 5-30% of original oil in place (OOIP). This method has several advantages, including improving oil recovery by minimizing residual oil saturation, decreasing water output from oil well, and requiring less water compared with water flooding.

Since the use of polymer flooding in the EOR activities, there is a lot of potential that biopolymer can play a significant role in improving oil recovery and getting all out of the current energy crisis. Biopolymer have big potential for polymer flooding have shown some advantages, such as eco-friendly materials; shear, salinity, and temperature resistance; and long-term stability. There are some studies to improve biopolymer's properties, such as modification biopolymers with nanoparticles or modification biopolymers grafting with synthetic polymers. The modified biopolymers effectively increase the efficiency of biopolymers for EOR under the reservoir conditions. Native biopolymer recovered additional oil from 27 until 62%. Meanwhile, modification of biopolymer increased additional oil recovery up to 71%. The use of modified biopolymers can make the EOR process greener and more facile.

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