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КҮКІРТ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕ «Ti-Cu» ЭЛЕКТРОДТАРЫН ҚОЛДАНА ОТЫРЫП АЙНЫМАЛЫ ТОК АРҚЫЛЫ ПОЛЯРИЗАЦИЯЛАУ КЕЗІНДЕ МЫС ҰНТАҚТАРЫНЫҢ ҚАЛЫПТАСУЫ

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Тірек сөздер: электрохимия, мыс, титан, айнымалы ток, поляризация, ұнтақ, осциллограмма.

Аннотация. Мақалада құрамында мыс (II) иондары бар күкірт қышқылы ерітіндісінде айнымалы токпен поляризацияланған мыстың электрохимиялық еруі және оның ұнтақтарын алу бойынша ғылыми мәліметтер келтірілген. Мыс электродының электрохимиялық еруіне және мыс ұнтақтарының түзілуіне электролиз параметрлерінің, яғни титан және мыс электродтарындағы ток тығыздығы, күкірт қышқылы мен мыс (II) иондарының бастапқы концентрациясы және айнымалы ток жиілігінің әсерлері қарастырылып, бұл процестер жүруінің оңтайлы шарттары табылды. Мысты күкірт қышқылы ерітіндісінде айнымалы және синусоидалы импульсті токтармен поляризациялау барысында түсірілген ток амплитудасы мәнінің уақытқа тәуелді өзгеруінің осциллограммалары келтірілді. Жиілігі 50 Гц болған өндірістік айнымалы токты қолданған кезде мыс ұнтақтары түзілуінің (57,9 %) және мыс электроды еруінің (77,9 %) максималды ток шығымдары байқалады, сондықтан осы ток жиілігі оңтайлы шарттардың бірі болып табылатындығы көрсетілді.

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MATHEMATICAL MODELING AS A TOOL FOR OIL SPILL EMERGENCY RESPONSE: CASE STUDY OF KASHAGAN OIL FIELD, KAZAKHSTAN

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Key words: Kashagan, oil spill, oil field, spreading, evaporation, emulsification, mathematical modeling.

Abstract. Oil spills are dangerous to the environment. Kashagan, one of the biggest oil fields in Caspian Sea, have high probability to release oil contaminations to the sea. In case of emergency situations, we must be ready to

understand how and in which direction oil slicks will move. Since remote sensing or tracking these spills from satellite at every hour are expensive, most reliable tool becomes mathematical modeling. Correct mathematical modeling might tell what will happen to the oil slick after desired hour and where it goes. The current paper, considers mathematical modeling of advection-diffusion of oil slicks, which also takes into account significant chemical and physical processes that change the properties of the oil slick and behavior of the oil slick in marine environment. The mathematical model is validated by comparing the results with the model developed by Comsol Multiphysics.

Introduction. Caspian Sea is becoming one of the potential oil fields in the world. In the Kazakhstan part of the Caspian Sea which is north-east there are several oil fields but one of the biggest fields is Kashagan. The field was discovered in 2000 and is planned to produce up to 1.5 million barrels per day in 2020. Such intensive oil production would make it as one of the biggest fields in the world and Kazakhstan would become one of the world's top oil-producing countries. However, chemical composition of the oil, which contains very high level of sulfur and other hazardous components such as mercaptans, exploration conditions with high pressure, offshore location and harsh climate, make Kashagan oil field dangerous to fragile ecosystems of the Caspian Sea and to its environment [1]. According to the information of the NGO Kaspiy Tabigaty, oil producing companies willing to drill about 240 wells in the field, which means there will be a high probability of crude oil spills. In worst cases, oil spills may be far more hazardous than those in the Gulf of Mexico where the depth of the drilled wells is about 1.5 km while Kashagan oil field is only 4-5 m below the Caspian Sea (Figure 1). Therefore, we must be ready to any disaster that could appear near Kashagan field.

Various earth observing and weather satellites such as RADARSAT or UARS help remote sensing of oceans and seas, and detect contaminations in them. However, by remote sensing it would be expensive in terms of economy to track every contamination such as oil spills over a sea surface at every time. Instead, correct mathematical modeling of spilled oil behaviour would be less expensive and effective respect to time [2].

a) b)

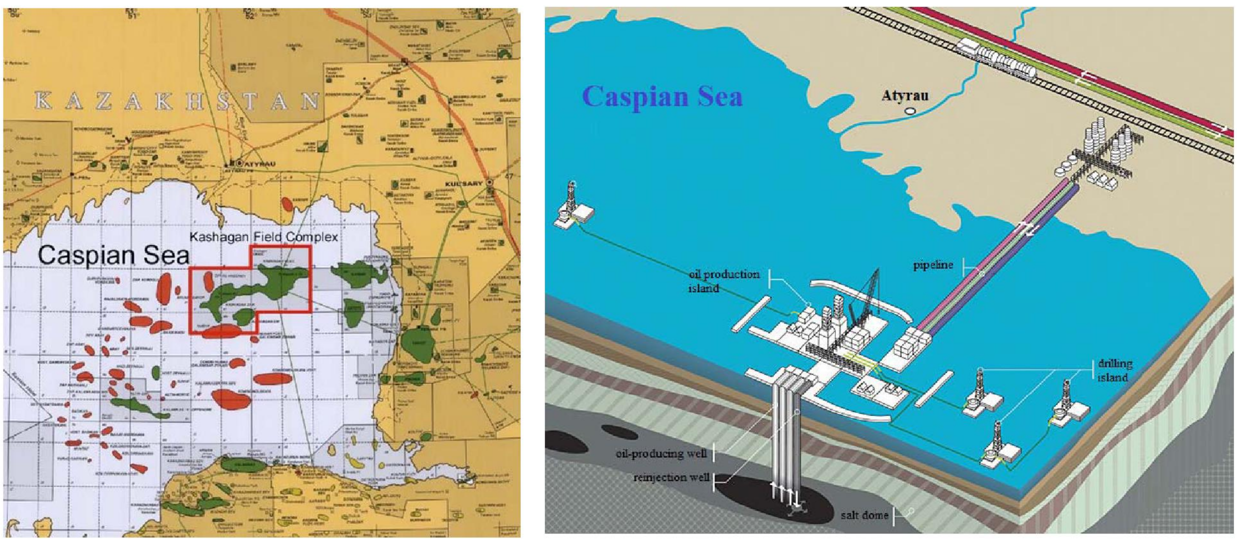


Figure 1 – a) Map of Kashagan oil field; b) Demonstration of oil producing and drilling islands of Kashagan offshore oil field

Oil properties. The crude oil is the mixture of hundreds of different organic compounds where each has its unique characteristics. Hydrodynamic behavior of spilled crude oil depends on physical and chemical properties of the oil and also on the environment properties [3].

Whether the spilled oil will float or sink is defined by a scale developed by Americal Petroleum Institute. It is the API gravity and it is inversely proportional to the specific gravity of the oil.

$$^{0}API = \frac{141.5}{specific\ gravity} - 131.5 \quad (1)$$

$$specific\ gravity = \frac{density\ of\ subs\tan ce}{densityof\ H_2O} \quad (2)$$

The specific gravity of the crude oil is calculated as ratio of oil density to fresh water density which has a specific gravity equal to 1. Therefore, API of the fresh water is 10. Most of the crude oils have a specific gravity of about 1.025 and higher API than 10, and float in fresh water. At initial PVT conditions, the specific gravity of the Kashagan oil varies between 574-619 kg/m^3, and API gravity of Kashagan oil starts from 43.36 to 45.76. It can be noticed that the crude oil from Kashagan field is light (API>10) and tend to float over the sea surface. According to the sulfur content (0.68 - 0.90 mass %), Kashagan oil belongs to Class II. Moreover, water mass fraction of this oil varies from 0.01 to 0.2%. The following figure compares the Kashagan oil with other ones respect to sulfur content and API gravity [4].

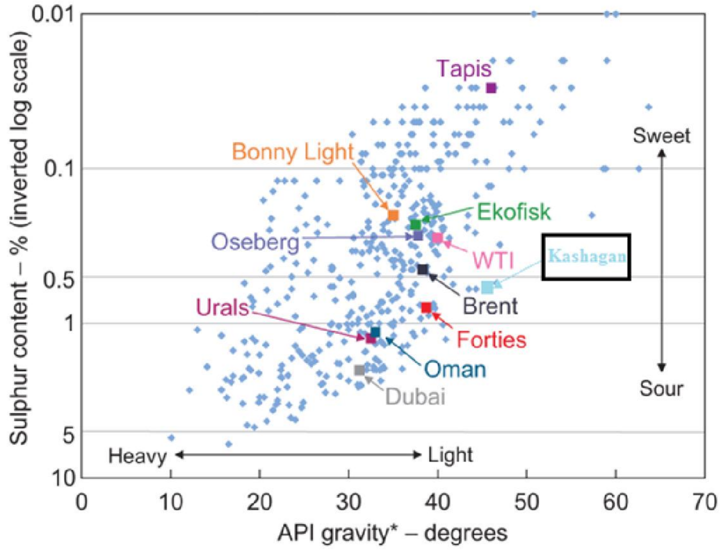


Figure 2 – Crude oils by density and sulfur content

Once oil discharged onto the water surface, several chemical and physical processes affect it. They are usually, emulsification, evaporation, dissolution, biodegradation, dispersion, and sedimentation, where some of them are controlled by oil properties. These processes dominate at different times following the oil spill and thus leading to loss of oil mass. It can be seen from figure 1 that processes such as evaporation, dispersion, emulsification and spreading affect to the oil slick right after it spilled to the sea, and have more influence to change the oil properties than dissolution, oxidation, biodegradation and sedimentation [5]. In this paper we are mostly interested in early time chemical and physical processes that significantly change the oil properties, for instance, viscosity, density, water fraction in oil and composition.

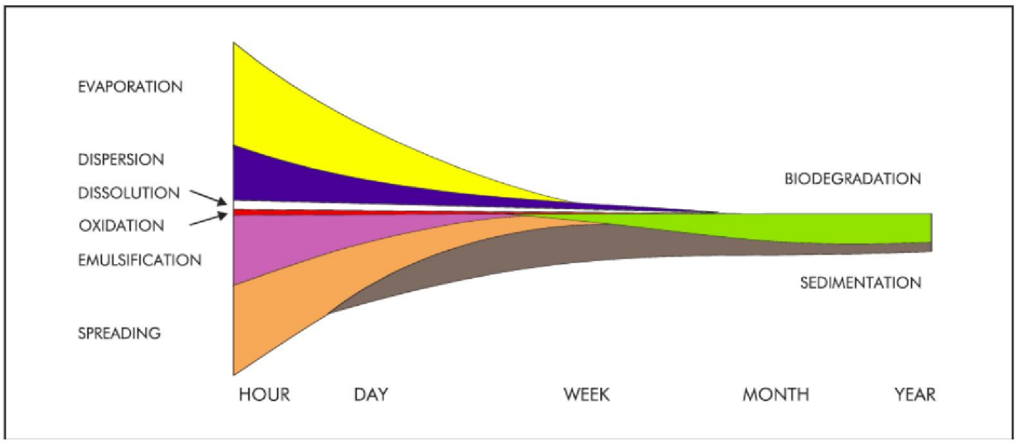


Figure 3 – Time dependence of the processes that affect to oil spills

Spreading. Once oil spilled, it spreads while floating over the sea surface. The rate of surface area change has been studied by Fay [6], Hault [7], and later modified by Mackay at al. [8]. Thus, the rate of surface area change is calculated by the following formula:

$$\frac{dA}{dt} = K_{Spread} \cdot A^{\frac{1}{3}} \cdot \left[\frac{V}{A}\right]^{\frac{4}{3}} \tag{3}$$

where A – area of the slick, $K_{Spread} = 150s^{-1}$ – constant, V – volume of spilled oil.

Evaporation. It is one of the early time processes that causes significant mass loss in all kinds of oil which has API>10. Moreover, it can significantly change density, viscosity and other properties. Most of the time, evaporation is responsible up to 60 percent of spilled oil mass loss [korotenko]. As the lighter components of the oil slick evaporates faster than heavier components, chemical composition of the slick changes. There are two famous methods applied to calculate an evaporation rate: a) the pseudo-component method [9-10], and b) the analytical approach [11]. The pseudo-component approach uses oil as a set of fractions grouped by boiling point and molecular weight. Consequently, for different components, there are different evaporation rates. On the other hand, in the analytical approach vapor pressure is a function of evaporated fraction. In this work, the analytical method developed by Stiver and Mackay [10] is applied to calculate volume fraction evaporated:

$$F_E = \ln\left[1 + B(T_G/T_E)(K_E \cdot A_S \cdot t/V_0)\exp(A - B(T_0/T_E))\right]\left[T_E/(BT_G)\right] \tag{4}$$

where F_E - evaporated volume fraction, $K_E = 2.5 \cdot 10^{-3} \cdot U_{wind}^{0.78}$ mass transfer coefficient for evaporation (m/s), U_{wind} - wind speed (m/s), V_0 - initial volume of oil spill (m^3), T_0 – initial boiling point (K) when F_E is zero (K), T_E – environmental temperature (K), T_G – gradient of the boiling point, T_B и T_E line (K), A and B are constants which can be chosen from distillation data. According to Stiver and Makay's calculations where they used distillation data for five different types of crude oils, magnitude of A and B are 6.3 and 10.3 respectively.

Dispersion. Turbulent wave energy can disperse the oil slick into cloud of droplets since oil may not dissolve in water. Droplets are in various size and are subjected to turbulent and buoyancy forces. For slicks with low viscosity under high sea conditions, dispersion can remove or displace about 90% of surface slick. The following expression is mostly used to calculate the dispersion, which is proposed by Reed and Mackay [11]:

$$D = 0.11(U_{wind} + 1)^2 / (1 + 50\mu^{1/2} h_s s_t) \tag{5}$$

where s_t - interfacial tension between oil and water (N/m), h_s - slick thickness (m), μ - viscosity (cp), U_{wind} - wind speed (m/s).

Emulsification. The process of emulsification is the inverse of dispersion where instead of oil droplets dispersing into the water column, water enters into the oil. As a consequence of the emulsification, volume, density and especially viscosity of oil slick changes. Mackey et al. suggested the following formula to calculate the incorporation of water into oil slick:

$$\frac{dF_{wc}}{dt} = K_{wc}(U_{wind} + 1)^2 (1 - F_{wc}) / OC \tag{6}$$

F_{wc} - fraction of water in oil, OC - final fraction of water content and K_{wc} is taken as 2×10^{-6}.

Density and viscosity. As already mentioned above, evaporation and emulsification are the main processes that change the density and viscosity of the oil slick. The following formulas are broadly used to calculate these changes:

$$\rho = F_{wc}\rho_w + (1 - F_{wc})(\rho_{ref} + C_{E2}F_E) \tag{7}$$

$$\mu = \mu_{ref} \exp(C_{E1}F_E + (C_{wc1}F_{wc})/(1 - C_{wc2}F_{wc})) \tag{8}$$

Mathematical model. Mathematical modeling of the oil slick movement over the surface, which takes into account significant chemical and physical processes, is not an easy task. The following paper uses advection-diffusion equation by taking into account vorticity in the flow, that is, vorticity transport equation [12].

$$\frac{\partial\Omega}{\partial t}+u\frac{\partial\Omega}{\partial x}+v\frac{\partial\Omega}{\partial y}=\nu\left(\frac{\partial^2\Omega}{\partial x^2}+\frac{\partial^2\Omega}{\partial y^2}\right) \quad (9)$$

where Ω - vorticity, which can be used to calculate the velocity potential ψ.

$$\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=-\Omega \quad (10)$$

And, velocity field is calculated in the following way:

$$u=\frac{\partial\psi}{\partial y}, v-=\frac{\partial\psi}{\partial x} \quad (11)$$

The velocity field then is applied to evaluate the oil concentration movement over the sea surface:

$$\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}=D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}\right) \quad (12)$$

where C – oil concentration, D – diffusion coefficient. The computational domain is shown in the following figure. At the right bottom, there is a coast which is needed to see the adhesion of oil slick to the shoreline [13].

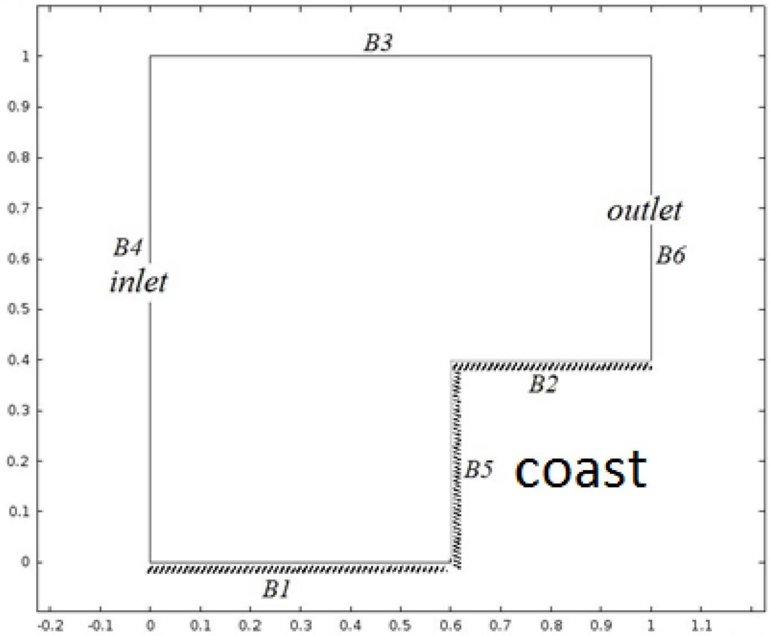


Figure 4 –Computational domain for verification of mathematical model correctness

Results and Discussions

To verify the correctness of the mathematical model, which takes into account all the chemical and physical processes, conditionally we take oil slick with initial area $Area_0 = 1664468m^2$ and initial volume $V_0 = 16645m^3$, and compare the results of advection diffusion of oil concentration with similiar model developed on Comsol Multiphysics.

a) b)

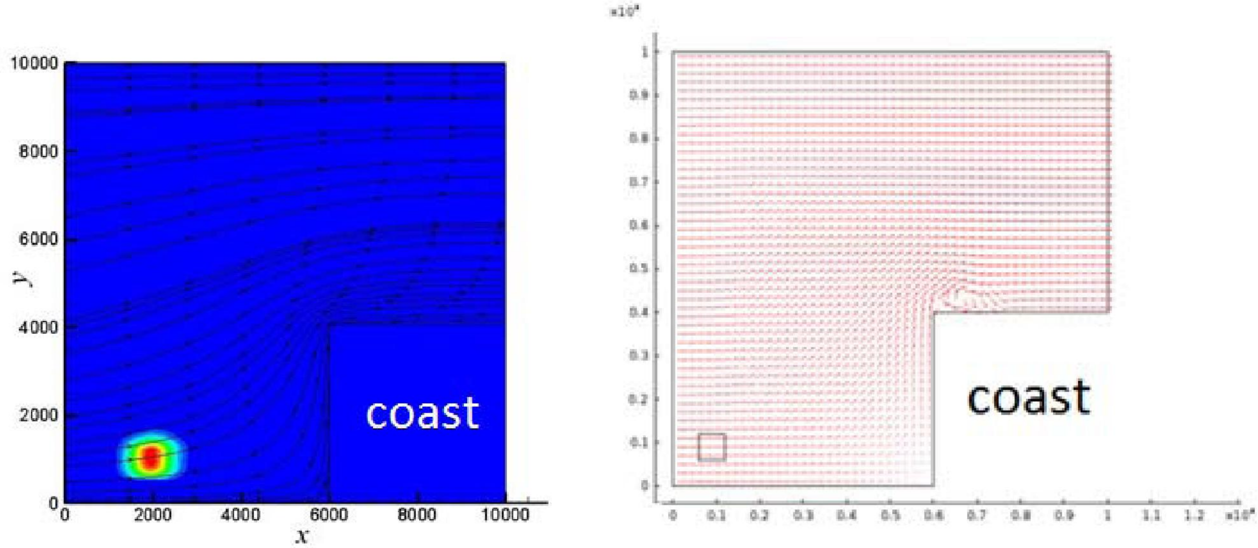


Figure 5 – Comparison of the velocity field between: a) Modeling; b) Comsol Multiphysics. t = 1200 sec

a) b)

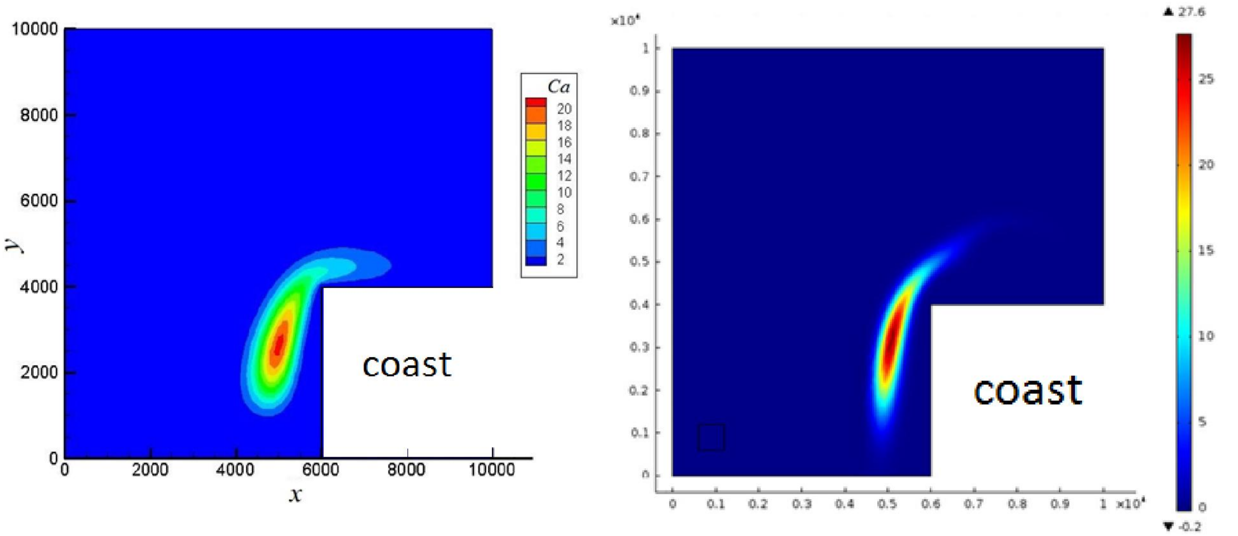


Figure 6 – Comparison of results at time t = 6000 sec: a) Modeling; b) Comsol Multiphysics

It can be noticed from the results that the mathematical model describes the movement of oil concentration and its adhesion to the shoreline with minimal errors. The above results are calculated by taking into account also the chemical and physical processes which effects to the properties of the oil slick. The following diagram shows how the authors calculated those processes:

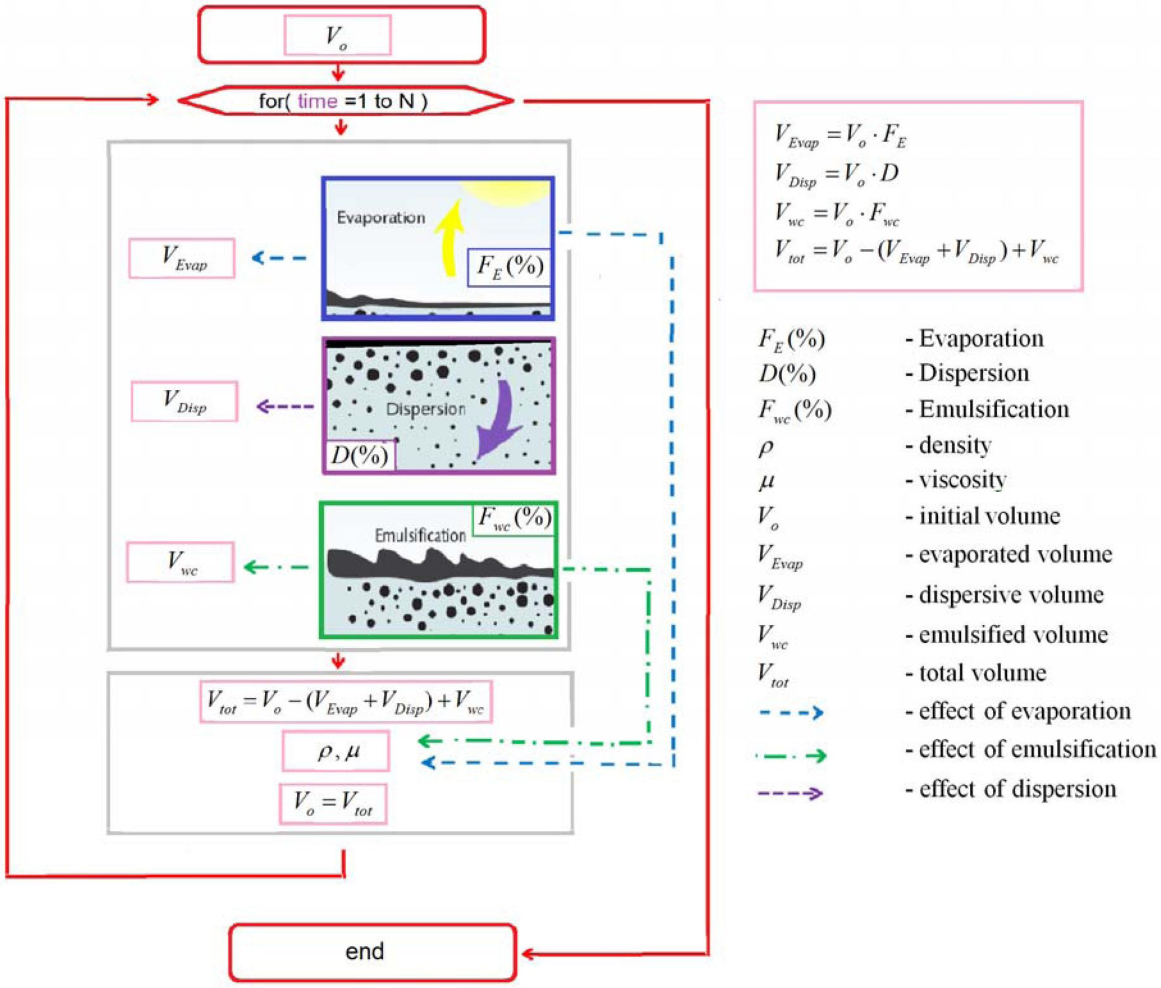
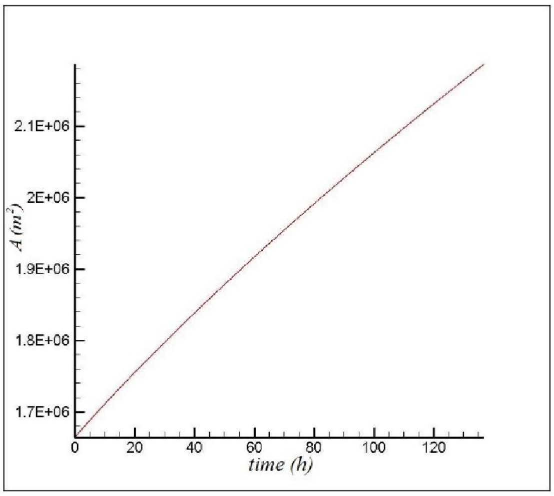


Figure 7 – The calculation order of chemical and physical processes that affect to the oil

Calculation of these processes are simultaneously done while calculating the advection-diffusion of the oil concentration, that is, solving equation (9)-(12). Moreover, time steps used for calculation of concentration movement is used for calculating chemical and physical processes such as spreading, evaporation, emulsification, dispersion and change of density and viscosity.

a)



b)

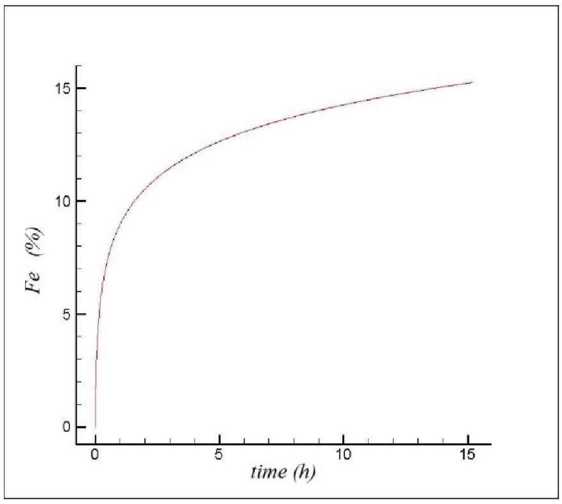


Figure 8 – Spreading and evaporation of the oil slick as a function of time (h)

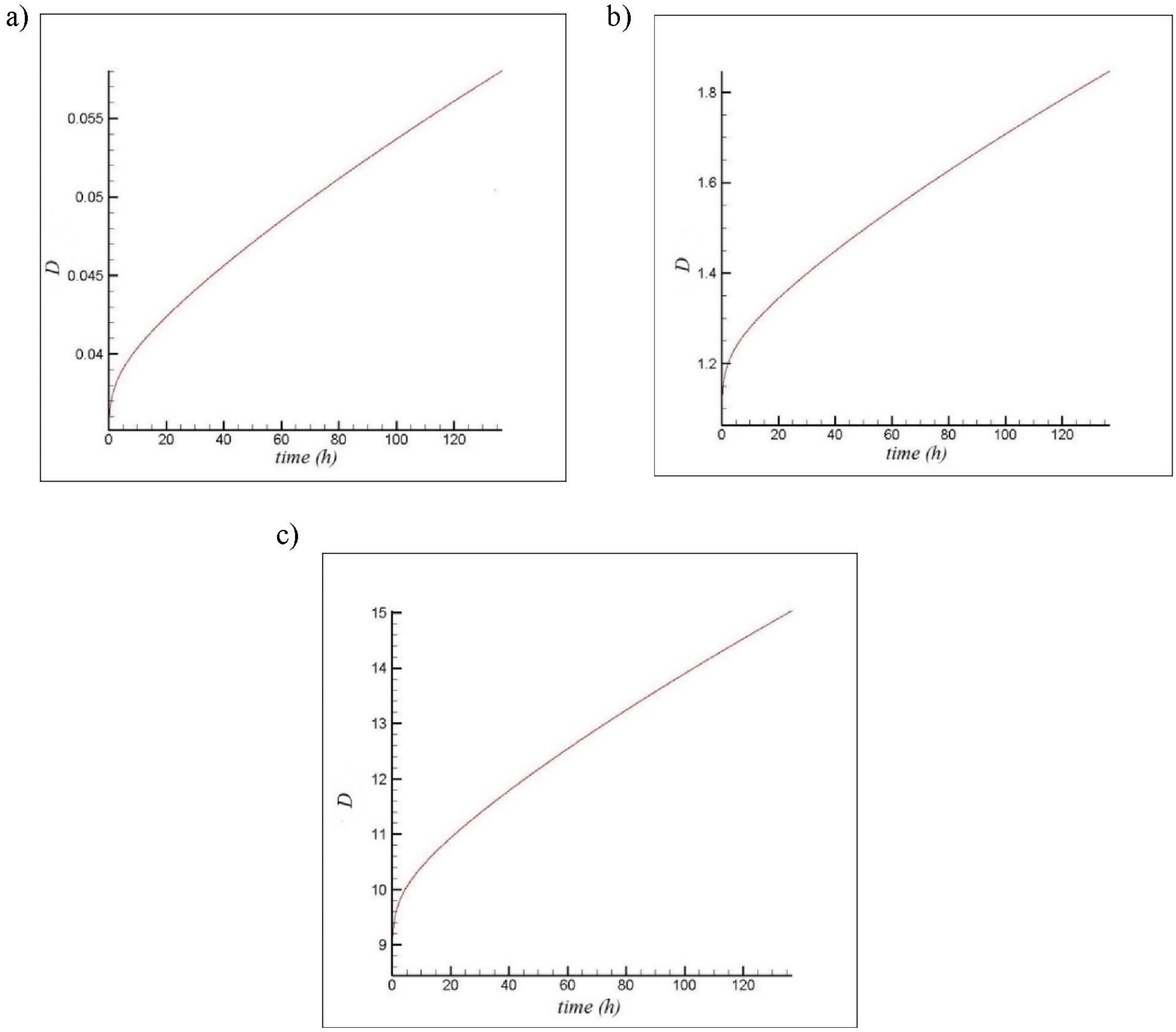


Figure 9 – Dispersion of oil slick as a function of time for different wind velocity: a) $U_{wind} = 1\ m/\sec$; b) $U_{wind} = 5\ m/\sec$; c) $U_{wind} = 10 m/\sec$.

In order to calculate above mentioned chemical and physical processes, Kashagan oil properties are considered. The initial viscosity is $3.66\ mm^2/\sec$ and the density is $796.8 kg/m^3$. The concentration of oil is considered to be 100% at initial time. According to the formula used to calculate the evaporation, there is a wind velocity in the mass transfer coefficient. And, it is true that the velocity is one of the main processes that accelerate the mass transfer, consequently, the evaporation process. Emulsification and dispersion are also dependent from wind velocity and the results from figures (9)-(10) verifies it. The results in figure (10) also shows that the emulsification does not exceed the maximum water content of Kashagan oil and this process is one of the early time processes since after several hours the slope of the curve does not change. The density and the viscosity are also change fast just after oil spill occurred, but slow down over time. And, after some time stop changing their value.

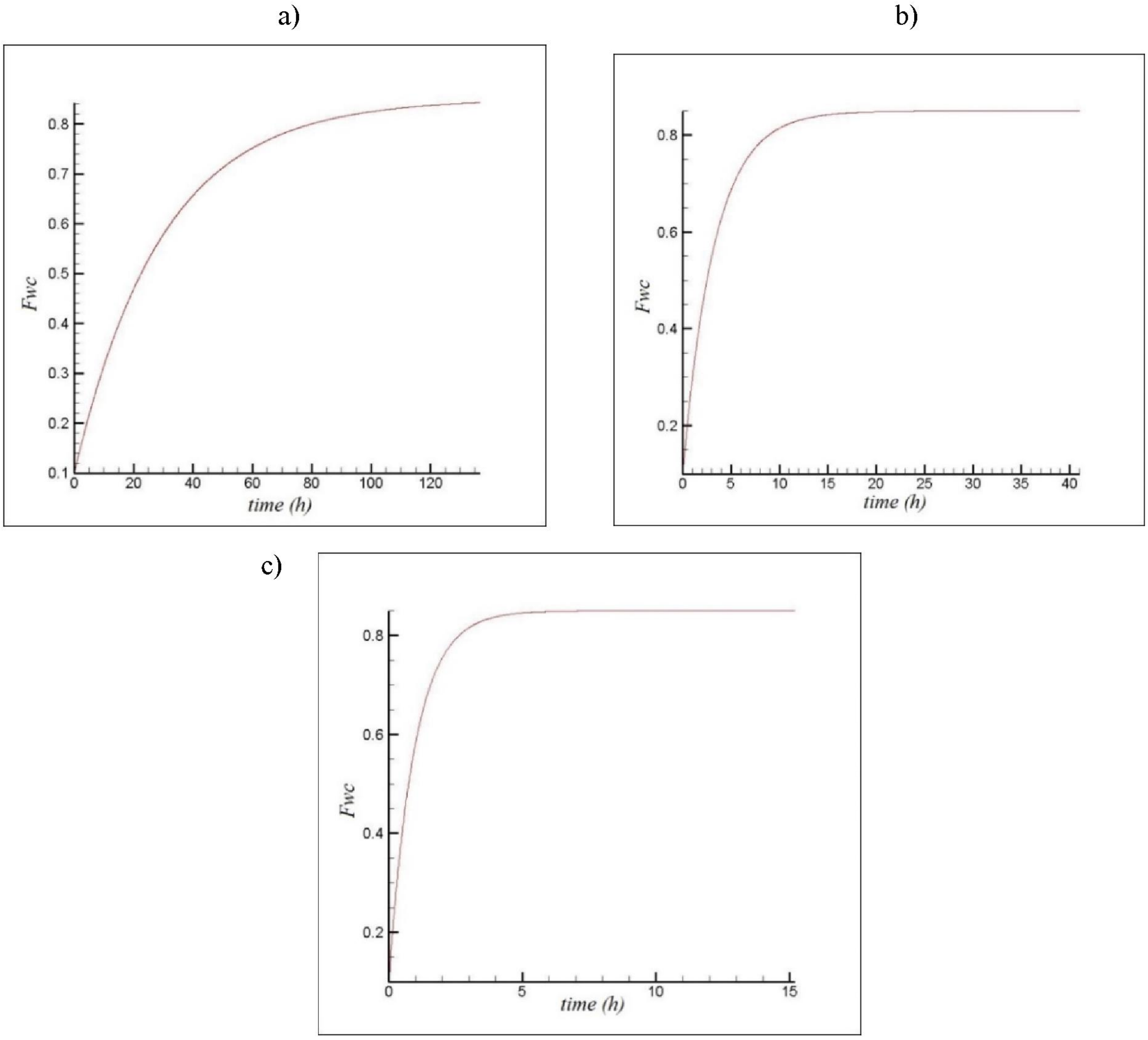


Figure 10 – Emulsification of oil at different wind speed:

a) $U_{wind} = 1\ m/\sec$; b) $U_{wind} = 5\ m/\sec$; c) $U_{wind} = 10 m/\sec$

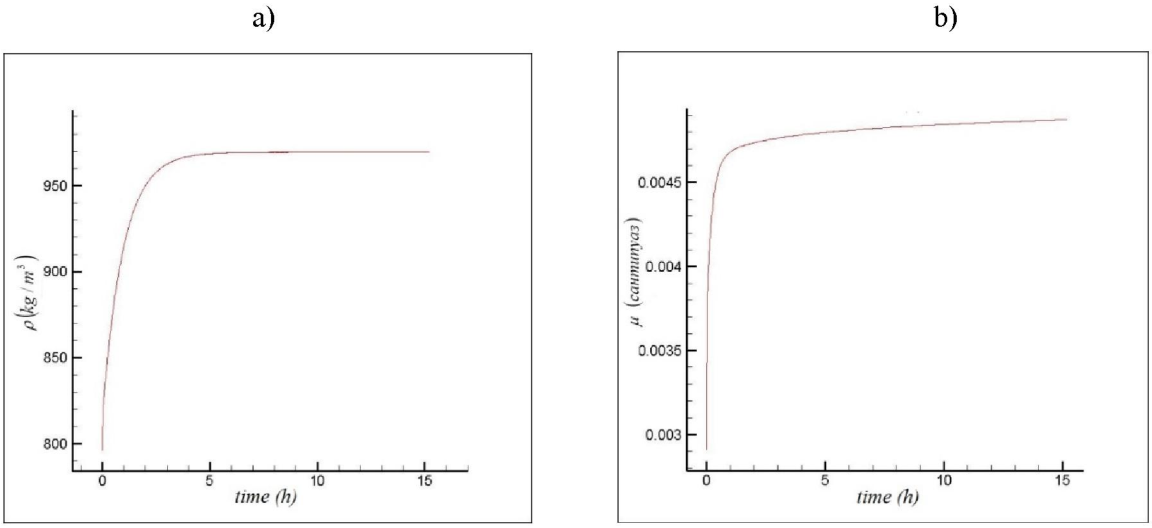


Figure 11 – Change of density and viscosity while oil slick is changing its position

Conslusion and future work. Last years, the oil drilling boreholes are becoming more near offshore oil field of Kashagan. The tectonic structure of the oil field itself tend to release oil spills naturally since it is underlies only about several meters below the sea. In case of emergency, behavior of oils slicks over the sea must be predicted in advance. One of the ways to predict the direction of the oil slicks is to use mathematical modeling.

In this paper, properties of Kashagan oil field are considered and used for calculating the chemical and physical processes that take place during oil slick floating lifetime.

Mathematical model based on vorticity transformation method is studied and applied for calculation of the velocity field. The velocity field then applied into the advection-diffusion equation to predict the oil slick movement. The model is validated by comparing the results with the model developed in Comsol Multiphysics.

The processes that cause the change in oil properties are studied and analyzed. These processes are concluded to be early time processes because they affect significantly to the oil slick at the beginning, but over time their influence decrease. In this paper, only the processes such as spreading, evaporation, emulsification, and dispersion are considered since they are the most significant ones that cause the change in oil properties.

Lastly, change of oil density and viscosity is studied and noticed that they mostly change because of above mentioned chemical and physical processes caused by marine environment.

There are many mathematical models exist that predicts the oil slick direction and change its properties. Although, they are advanced they are not suitable to predict the oil spills in Kazakhstan part of the Caspian Sea. In a word, there is no universal model or simulator that could predict oil slick movements in every sea or ocean since each sea has its unique environmental parameters. This paper results are one of the parts of the oil spill simulator that is being developed for Kazakhstan part of the Caspian Sea. In the future, the model will be developed and strengthened applying advanced numerical techniques and developing complicated computational mesh for the Kazakhstan part of the Caspian Sea. Moreover, more chemical and physical processes are going to be taken into account to improve the mathematical model.

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ҚАШАҒАН МҰНАЙ КЕН ОРНЫ ҮШІН, ТЕҢІЗ БЕТІНДЕГІ МҰНАЙ ДАҚТАРЫНЫҢ ҚОЗҒАЛЫСЫН ЖӘНЕ ӨЗГЕРІСІН МАТЕМАТИКАЛЫҚ МОДЕЛЬДЕУ

Б. Е. Бекмұхамедов, Б. Д. Ахметов, Ж. Ш. Жантаев

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Аннотация. Мұнай қалдықтары қоршаған ортаға қауіпті. Қашаған мұнай кен орны , Каспий теңізіндегі ірі мұнай кен орындарының бірі болуы себепті, Қашаған мұнай кен орнының теңізді мұнай қалдықтарымен ластау ықтималдығы жоғары. Апат орын алғын жағдайда, теңіздегі мұнай дақтарының қалай және қай

бағытта қозғалатынын білу маңызды. Теңіз бетіндегі мұнай дақтарының қозғалысын дистанционды (қашықтан) зондау немесе жер серіктері арқылы бақылау қымбат болғандықтан, бақылаудың тиімді құралы математикалық модельдеу болып табылады. Мұнай дақтарының қозғалысын және өзгерісін дұрыс математикалық модельдеу арқылы әр сағаттағы керекті ақпарат пен мұнай дақтарының теңіз бетіндегі орнын анықтай аламыз. Аталған мақалада ковективті-диффузияланатын мұнай дақтарының математикалық моделі қарастырылады, сондай-ақ, теңіздегі мұнай дақтарының физикалық қасиеттеріне және мұнай параметрлерінің (көлемінің, ауданының) өзгерісіне әсер ететін маңызды физикалық және химиялық процесстер де ескеріледі. Нәтижелер, COMSOL Multiphysics программалық пакетінде алынған нәтижелермен салыстыру арқылы тексерілген.

МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ КАК ИНСТРУМЕНТ ДЛЯ ПРОГНОЗА АВАРИЙНОГО НЕФТЯНОГО РАЗЛИВА: КАШАГАНСКОЕ МЕСТОРОЖДЕНИЕ, КАЗАХСТАН

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Аннотация. Нефтяные разливы опасны для окружающей среды. Кашаган, один из крупнейших нефтяных месторождений в Каспийском море, имеет высокую вероятность выбросов нефтяных загрязнений на море. В случае чрезвычайных ситуаций, мы должны быть готовы, в каком направлении нефтяные слики будут двигаться. С дистанционного зондирования или отслеживания этих разливов со спутника, например, каждый момент времени будет стоит дорого, а самым надежным инструментом становится математическое моделирование. Правильное математическое моделирование может прогнозировать движения и трансформации нефтяных пятен на поверхности воды в нужное время. В этой статье авторы рассматривают конвекционно-диффузионное уравнение для изучения движения концентрации нефти на поверхности мелководной воды с учётом важных химико-физических процессов, которые в течение времени влияет на свойства нефти и на поведение нефти в водной среде. Результаты моделирования были сравнены с результатами модели, созданной в Comsol Multiphysics - пакет моделирования для решения задачи из естественных наук.

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THE INFLUENCE OF ELECTROMAGNETIC SCHUMANN RESONANCES ON THE BRAIN RHYTHMS DURING SLEEP

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Abstract. Interest in the impactof magnetic field on activity of brain rhythms arose during the study of the phenomenon of lucid dreams. Our task was to determine whether there are external environmental factors that affect brain functioning, in particular to the quality of sleep. In this article we present the research results of the relationship between brain rhythms activity and the variability of the geomagnetic field near the earth's surface. In the process, we compare the time dependence of the quality of sleep and the time dependence of the A_P-index(daily average geomagnetic activity). It is revealed that in the night time the magnetic field affects the activity of brain rhythms. We assume that the intensity of the magnetic field depends on the amplitude of the electromagnetic Schumann resonances.