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Present Situation of Coal Combustion By-products Utilisation in Mongolia and Challenges

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Abstract

Coal combustion by-products are generally divided into fly ash, bottom ash and flue gas desulfurization waste. Globally, thermal power stations are producing over 600 million tonnes of fly ash per year of which only 25% is utilised. Pond ash is weathered ash which was deposited into an ash pond or lagoon by wet or dry methods comprising fly ash and/or bottom ash in variable proportions. Traditionally fly ash is mostly used in the production of cement, concrete and geopolymers.

Several Mongolian fly ashes and pond ashes were evaluated by XRD, XRF, particle size analysis, BET, SEM, TEM and gamma spectroscopy methods. Here we report the latest results on the preparation of geopolymer type concrete, light-weight gaseous concrete and bricks from fly ash and pond ashes. TEM and BET methods revealed that pond ashes have a porous and agglomerated microstructure. The specific surface area of pond ash was about ten times higher than fly ash because of the partial dissolution of soluble compounds into the pond water.

Geopolymer-type concrete produced at semi pilot scale indicated that the quality of produced products was comparable with those prepared with ordinary Portland cement (OPC).

As-received pond ash was used in the preparation of geopolymer-type light-weight concrete with products achieving a compressive strength of 3.17 MPa and volume weight of 900 kg/m^3. Pond ash mechanically activated for 30 min. was also used in geopolymer-type paste preparation which resulted in a product with a compressive strength of over 15 MPa.

Use of fly ash and pond ash in the production of geopolymer-type paste, mortar, concrete and lightweight gaseous concrete has been demonstrated. These uses substantially reduce greenhouse gas emissions and decrease the environmental problems associated with the long term storage of ashes deposited into ponds.

Keywords: coal combustion by-products, characterization, radioactivity, building materials, geopolymers, light-weight concrete, microstructure

Современное состояние и проблемы утилизации побочных продуктов сжигания угля в Монголии

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Аннотация

Побочные продукты сжигания угля обычно делятся на летучие золы, шлаки и отходы от сероочистки дымовых газов. Мировые тепловые электростанции ежегодно производят более 600 миллионов тонн летучей золы, из которых используется только 25%. Влажными или сухими способами летучие золы улавливаются и в итоге задерживаются в прудах или бассейнах и такие «прудовые золы» содержат летучую золу и/или шлак в различных пропорциях. Традиционно в производстве цемента, бетона и геополимеров в основном используются летучие золы.

Несколько летучих зол и осадочных зол из водоемов Монголии оценивались методами рентгеновской дифракции, РФА, анализа размеров частиц, БЭТ, СЭМ, ТЭМ и методами гамма-спектроскопии. ТЭМ и метод БЭТ показали, что прудовые золы имеют пористую и агломерированную микроструктуру. Удельная площадь прудовой золы была примерно в десять раз больше, чем у летучей золы вследствие частичного растворения в водоеме растворимых соединений. В этой работе мы сообщаем о последних результатах по приготовлению бетона геополимерного типа, легковесных газобетона и кирпичей из летучей золы и прудовых зол.

Бетон геополимерного типа, полученный в полупромышленном масштабе с использованием прудовой золы, оказался сопоставимым по качеству с бетоном, изготовленным из обычного портландцемента. Прудовая зола без дополнительной обработки использовалась в приготовлении легкого бетона геополимерного типа с прочностью на сжатие достигавшей 3,17 МПа и с объемным весом 900 кг/ м^3. Прудовая зола механоактивированння в течение 30 минут был также использована в приготовлении пасты геополимерного типа, что привело к получению продукта с пределом прочности при сжатии более чем 15 МПа.

В работе продемонстрировано использование летучей золы и прудовой золы в производстве пасты геополимерного типа, строительного раствора, бетона и легкого газобетона. Такое использование позволит существенно сократить выбросы парниковых газов и уменьшить экологические проблемы, связанные с длительным хранением золы, депонированной в водоемы.

Ключевые слова: побочные продукты сжигания угля, характеризация, радиоактивность, строительные материалы, геополимеры, легкий бетон, микроструктура

1 Introduction

In the 1920's the terms fly ash and bottom ash began to be used after installation of more efficient combustion equipment [1]. Depending on the coal type, impurities and a power plant's operation, up to 30% of inorganic constituents of the original coal reports to by-products [2]. The main coal combustion by-products are fly ash which is separated from the flue gas and bottom ash which is collected from the bottom of the boilers. The chemical and mineralogical compositions of the ash change primarily due to variations in the feed coal. The mineralogical composition may also differ with season and electricity demand at the time of the power production with high demand resulting in the coal burning at lower temperature thus changing both ash mineralogy and unburnt carbon content.

Coal combustion by products is considered to be among the most abundant wastes in the world with 650 to 750 million tonnes produced annually [3, 4]. The worldwide average utilization rate of coal combustion by-products is approx. 25%. The unused fraction is likely to be deposited into an ash pond and stored. There is strong interest in recycling these coal combustion by-products because of their abundance and environmental problems caused by keeping these ashes in the ash pond. For instance, in 2008 in the US, 42.3 million tons of ash was landfilled. It was estimated that 100 to 500 million tons of ashes have been stockpiled in United States landfills since the 1920s [5]. There are many reviews on sustainable ways to utilize ash products [2, 3, 6], but few methods have been adopted at significant scale.

In Mongolia, as in the rest of the world, the most utilized ash is fly ash. Previously it has been utilized for geopolymer type concrete production [7] and for preparation of geopolymer type binder materials [8].

In this report we summarize our latest results on utilization of coal combustion by products for preparation of geopolymer type concrete, mortar and light weight concrete.

2 Experimental

Ashes from the 4th Thermal Power Station (TPS) of Ulaanbaatar city were collected. The 4th TPS uses two sources of coal, Baganuur and Shivee ovoo. Fly ashes from both coals and pond ash were used as raw materials. Pond ash from the Darkhan city TPS was also examined.

Several different materials were prepared from the coal combustion by-products:

1. Preparation of geopolymer type binder materials from mechanically activated pond ash.
2. Preparation of lightweight gaseous concrete from pond ash.
3. Preparation of geopolymer type concrete from the fly ash.

For the geopolymer type binder, pond ash from Darkhan city TPS was mechanically activated in a planetary mill for up to 30 min, it was then chemically activated using 8M NaOH and finally cured at 70^{o}C for 20h [8].

Lightweight gaseous concrete was prepared from the pond ash of the 4th TPS of Ulaanbaatar city. Various ash and sand compositions were activated using 6, 8 and 10M NaOH solution and cured at 70^{o}C for 20h. Aluminium powder (75um) was added as 0.5% of the dry weight of ash+sand as the gas forming agent.

Geopolymer type concrete was prepared from Baganuur and Shivee ovoo fly ashes of the 4th TPS of Ulaanbaatar city. Fly ash samples were mixed with aggregates and activated using 8M NaOH solution and cured at 70°C for 20h. Detailed experimental procedures are shown elsewhere [7, 9].

The chemical composition of the ashes was determined by X-ray fluorescence (XRF) and specific surface area by BET analysis. The mineralogical composition of the fly ashes and synthesised samples was determined by X-ray diffraction (XRD). Morphology of fly ashes was observed by SEM and TEM. Radiation measurements were performed by gamma ray spectroscopy according to Mongolian standard MNS 5072:2001. Compressive strengths were measured with a universal testing machine (UTM). Densities of the specimens were measured by weight and geometric volume ratio.

3 Results and Discussion

3.1 Characterization of coal combustion by-products

The chemical composition of the different ashes is shown in Table 1. Table 1 indicates that there is some variation in chemical composition with time, the changing composition of the coal with time makes this inevitable. The XRD patterns of the Baganuur fly ashes (not shown) collected in 2011 and 2013 years were almost identical with relatively minor variation in the proportion of the phases present. XRD patterns of the Baganuur and Shivee ovoo fly ashes and as well as pond ashes from the 4th thermal power station and Darkhan power station are shown elsewhere [7, 8].

Table 2 shows BET surface area and pore volume of the ashes. From the BET data it can be concluded that pond ash has a higher specific surface area than fly ash, this can be attributed to partial dissolution of ash phases in the pond water resulting in a more porous structure for pond ash.

Table 1. Chemical composition of ash products (wt.%)

Power station	Coal/Ash source	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	SO_3	K_2O	SrO	TiO_2
Ulaanbaatar 4th power station	Shivee-ovoo, 2011	33.9	12.2	9.9	30.8	6.4	1.2	3.7	0.7	0.4	0.4
Ulaanbaatar 4th power station	Baganuur, 2011	55.2	14.2	10.6	15.0	1.6	0.3	1.2	1.3	0.3	0.3
Ulaanbaatar 4th power station	Baganuur, 2013	51.18	13.02	14.9	14.47	1.74	0.53	0.61	1.34	-	0.51
Ulaanbaatar 4rd power station	Pond ash	52.3	15.5	10.1	16.6	1.9	0.1	1.4	1.5	0.2	0.3
Darkhan TPS	Pond ash	51.2	28.6	11.0	3.4	1.7	-	0.3	1.7	0.1	1.5

Table 2. BET surface area and pore volume of ash samples

Sample name	Specific surface area, BET m^2/g	Pore volume, ml/g ($x10^{-3}$)
Fly ash, Shivee ovoo, 2011	1.04	1.49
Fly ash, Baganuur, 2011	2.75	2.12
Ash pond, 4rd TPS,	10.13	49.4
Darkhan TPS, ash pond	9.96	20.2

Fig.1 and Fig.2 shows SEM and TEM micrographs of the used fly ashes and pond ashes.

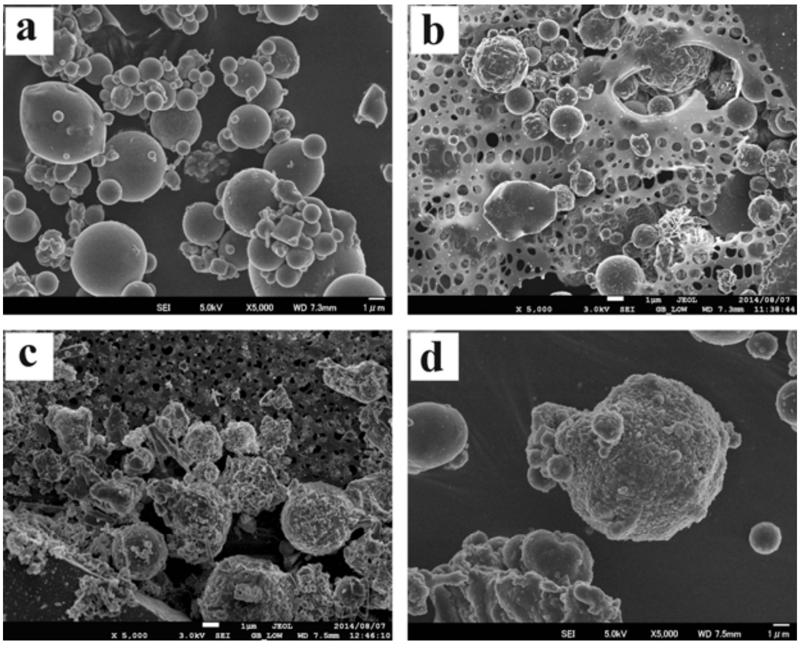

Figure 1: SEM micrographs of the (a) Baganuur and (b) Shivee ovoo fly ashes, and pond ashes from (c) 4th TPS and (d) Darkhan TPS

The SEM clearly shows the presence of <5um cenospheres in the fly ashes, these become noticeably rougher and more agglomerated in the pond ash samples. The roughening of the cenosphere surface is due to dissolution of soluble phases in the pond water and is commensurate with significant increase in BET surface area. The increase in agglomeration may be due to cementing of the spheres by precipitation of silica previously dissolved in the waters.

TEM micrographs fully support the SEM micrographs and BET data of the ash products. The rough surface of the cenospheres in pond ash is due to the presence of a semi transparent gel formed from the silica dissolved from the fresh ash. It is clear that in order to increase reactivity of the ash products, especially the low reactivity porous pond ashes, it is necessary to use some pretreatment, such as mechanical activation.

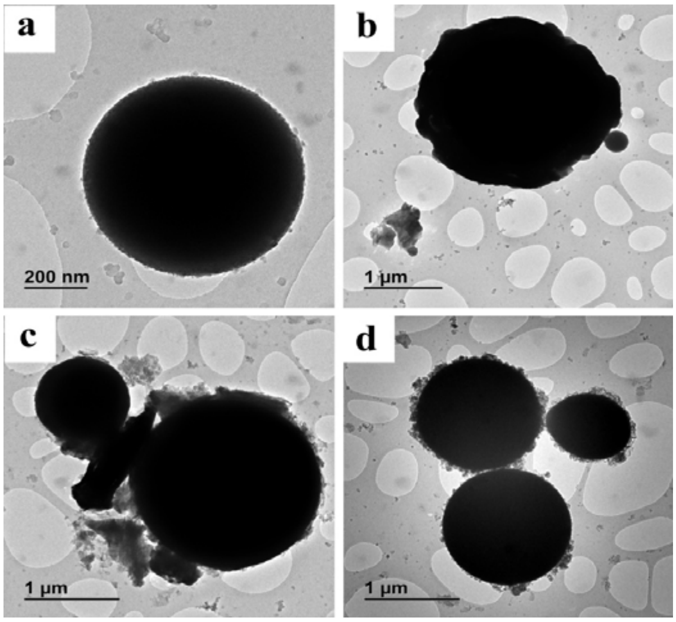

Figure 2: TEM micrographs of particles of the fly ash from (a) Baganuur and (b) Shivee ovoo and pond ash from (c) 4th TPS and (d) Darkhan TPS

3.2. Preparation of geopolymer type binder materials from mechanically activated pond ash.

Pond ashes from Darkhan TPS were milled for up to 30 minutes. Even the initial 5 min. of milling leads to a uniform low porosity microstructure. Moreover, mechanical amorphization of the crystalline phases in the pond ash was also observed [8].

Mechanical amorphization of the crystalline compounds was evaluated by measuring the crystallite size decrease of the mullite and quartz in the ash. An alkali-activated geopolymer-type paste milled for 5 minute showed the same compressive strength (~3 MPa) as raw pond ash. The geopolymer-type binder prepared from the 30 minute milled pond ash results increased compressive strength to 15 MPa. The higher strength with increasing milling time is could be explained by the higher extent of amorphization and low porosity of the ash samples leading to an increase in the cement phase formed upon alkali activation. Obviously, binder phase is more dense and low porous. less dense for the raw sample and more dense for the 30 min milled sample.

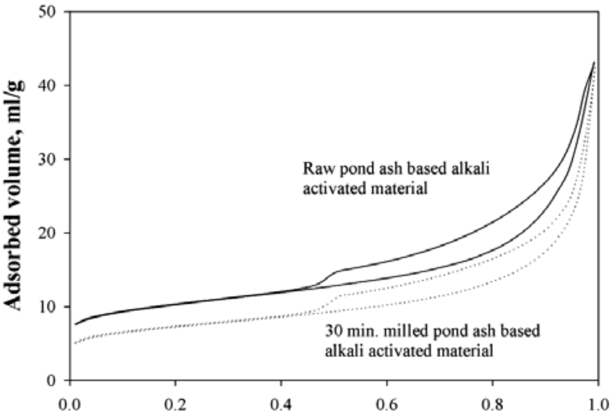

Figure 3: Sorption isotherms of raw and 30 min. milled pond ash based alkali activated material

The N_2 sorption-desorption isotherms (Fig. 3) for the raw sample and 30 minutes milled sample based alkali activated material indicates that the alkali activation of raw material lead to a cement of less density, i.e. higher surface area, compared to the 30 min milled samples which seems to be more dense with a smaller surface area.

Both specimens show hysteresis loops due to presence of mesopores, which are formed in the geopolymer network. The shape of the loops is same type for both specimens. But there is a difference between the two isotherms on the initial adsorption point. Raw pond ash based alkali activated materials clearly have more micropores than 30 minute milled pond ash based materials. Therefore, again the cement possessing higher strength is related to the formation with a lower concentration of micropores, i.e. a more dense material.

The higher density follows on from having a more compact structure due to improved packing of the particles leaving less void space.

Mechanical milling is one possible method for treating pond ash in order to prepare alkali activated materials with the acceptable mechanical properties.

3.3. Preparation of lightweight gaseous concrete from pond ash.

Lightweight gaseous concrete from the pond ash of 4th TPS preparation procedure was same as was for Darkhan pond ash based lightweight concrete [10]. Fig.4 shows change of the compressive strength with alkali solution concentration and ash:sand ratio.

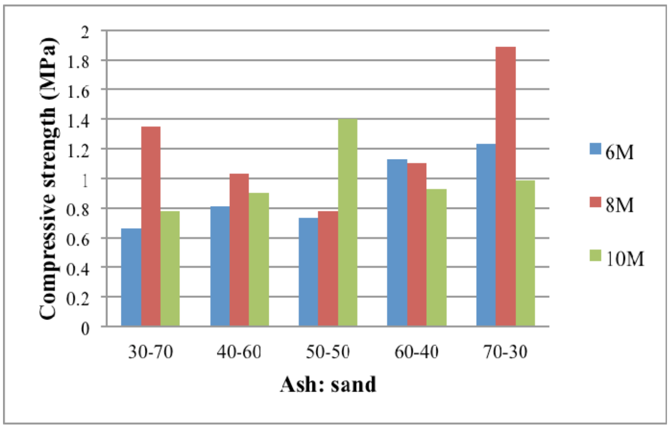

Figure 4: Change of compressive strength of lightweight concrete with ash:sand ratio

The general trend is that compressive strength increased with ash content. This behaviour is not-unusual because increased ash content will lead increased binder content in the lightweight concrete. The highest compressive strength was observed for the sample containing 70% ash and 30% sand activated with 8M NaOH solution.

The Al powder reacts with water in an alkaline environment liberating bubbles of hydrogen gas which form pores in the concrete, according to the following reaction:

$$Al_{(s)} + 3H_2O_{(l)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3/2\ H_{2(g)}$$

Therefore pore size should depend on the particle size distribution of the aluminium powder and the homogeneity of mixing throughout the mixture prior to activation.

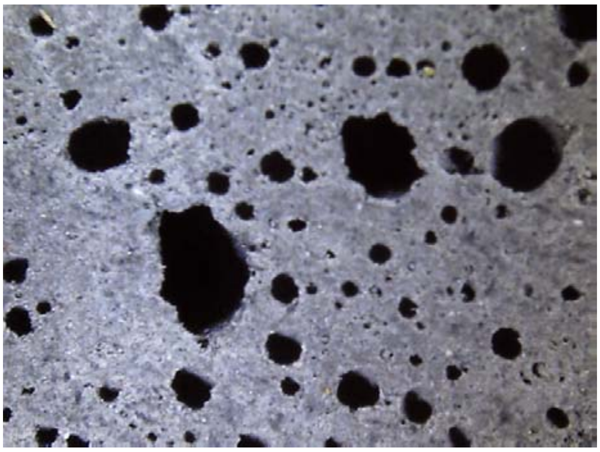

Figure 5: light micrograph of the lightweight concrete

Figure 5 shows a micrograph of a cut and polished section of concrete. Clearly, the pore size and pore distribution of the porous concrete was not uniform. A more effective method for homogeneous dispersal of the aluminum powder is required in order to produce porous concrete with uniform size and distribution of pores.

3.4 Preparation of geopolymer type concrete from the fly ash.

Geopolymer type concretes were successfully prepared from the Baganuur fly ash [7]. However, as discussed previously there is chemical and mineralogical composition variability of the fly ashes with collection times. A further important variable in the ash is the level of radionuclides, the range of end uses of the concrete may be limited by the radioactivity according to international standards.

Geopolymer concretes prepared from the Baganuur fly ash collected in 2011 show compressive strength of over 30 MPa, while from Shivee ovoo fly ash over 20 MPa. Baganuur fly ash collected in 2013 showed some changes in chemical composition, but mineralogical variation was small. Geopolymer type concrete prepared from the Baganuur fly ash in 2013 showed a compressive strength of 30 MPa. The detailed experimental procedure used has been described previously [7, 9]. Moreover, geopolymer type concrete from the 2013 was tested in outside environmental condition.

Fig.6 shows geopolymer type concrete kept outside during the 2013 to 2014 winter (Average temperature is -20^{o}C-25^{o}C). Practical use of geopolymer type concrete as paving block shows a quite well mechanical properties and freeze resistance. The main difference between the Baganuur fly ashes collected in 2011 and 2013 was radionuclide activity. There is almost a fourfold difference between the ashes. Table 4 shows isotope activity of used ashes and geopolymer type products. According to Mongolian standard MNS 5072:2002, radioactivity of building materials used indoor condition must be below 370 Bq/kg. Therefore, if prepare building material from the Baganuur fly ash collected in 2013 it must be below 370 Bq/kg.

Figure 6: Geopolymer type concrete after keeping outside in winter condition

For preparation of geopolymer type concrete was used gravel aggregate with an average size of 3.8 mm. Isotope activity of the geopolymer concrete prepared by addition of 80% of gravel aggregate reduced to 196 Bq/kg resulting in no hazard to human health.

Radiation characteristic of the coal combustion by-products is highly variable and can be at levels which are known to affect human health. However, the present research shows that it can be reduced by dilution of low radiation aggregates that dilute the ash's radiation.

Our results were supported with semi pilot scale production of geopolymer type concrete. Semi pilot scale produced concrete also showed compressive strength over 30 MPa.

Table 4. Isotope activity of ash samples and geopolymer concretes

№	Products	Isotope activity, Bq/kg			Radium equivalent (Ra_{eq}), Bq/kg
		A_{Ra-226},	A_{Th-232},	A_{K-40},	
1	Baganuur fly ash (2011)	242.4	31.1	381.6	314.4
2	Shivee ovoo fly ash (2011)	262.8	48.7	215.6	342.7
3	Baganuur fly ash (2013)	1169.2	26.9	355.1	1233.6
4	Geopolymer concrete based on Baganuur fly ash (2011), (ash 25% + aggregate 75%)	37.8	15.6	831.4	129
5	Geopolymer concrete based on Shivee ovoo fly ash (2011) (ash 25% + aggregate 75%)	54.8	17.2	884.9	152.6
6	Geopolymer concrete based on Baganuur fly ash (2013) (ash 20% + aggregate 80%)	119.2	13.1	697.9	195.7

Conclusion

Coal combustion by-products of the Mongolian thermal power stations represent potentially useful raw materials for building materials production. Chemical composition and radiation characteristics of the coal combustion by-products are not constant and vary significantly with time. From mechanically activated pond ash geopolymer type binder with compressive strength of 15 MPa can be prepared. Lightweight concrete prepared from pond ash with ash to sand ratio of 70:30 showed a compressive strength of 1.85 MPa and density of 1100 kg/m^3. There is little influence of chemical composition variation of fly ash on mechanical properties of the geopolymer type concrete. Radiation characteristics of the geopolymer building materials can be tailored with addition of low radiation aggregates.

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References

1. We Energies Coal Combustion Products Utilization Handbook, Ramme – Tharaniyil 3rd Edition, 2013
2. *Jha, V., Matsuda, M., Miyake, M.* Resource recovery from coal fly ash waste: an overview study, J.Ceram. Soc.Jap. 2008, 116: 167-175
3. *Ahmaruzzaman, M.* A review on the utilization of fly ash, Progress. Energy.Combust.Sci., 2010, 36: 327–363
4. *Blissett, R.S., Rowson, N.A.* A review of the multi-component utilisation of coal fly ash, Fuel, 2012, 97: 1–23
5. Perkins+Will, Fly ash White Paper, 54p. 2011
6. *Wang, S, Wu, H.* Environmental-benign utilisation of fly ash as low-cost adsorbents, J. Hazard. Mater.B, 2006, 316: 482-501
7. *Temuujin, J., Minjigmaa, A., Davaabal, B., Bayarzul, U., Ankhtuya, A., Jadambaa, Ts., MacKenzie, K.J.D.:* Utilization of

radioactive high-calcium Mongolian flyash for the preparation of alkali-activated geopolymers for safe use as construction materials, Ceram. Inter., 2014, 40: 16475–16483

8. *Temuujin, J., Minjigmaa, A., Bayarzul, U., Kim, D.S., Lee, S.H., Lee, H.J., Ruescher, C.H., MacKenzie, K.J.D.:* Properties of alkali-activated geopolymer binders from milled pond ash and the immobilization of their heavy metal contaminants, Advances in Materials Science and Engineering. submitted (2015)

9. *Temuujin, J., Minjigmaa, A., Zolzaya, Ts., Davaabal, B.*: Preparation and characterisation of geopolymer type paste and concrete from high calcium Mongolian fly ashes, Trans. Ind. Ceram. Soc., 2014, 73: 157-160

10. *Temuujin, J., Minjigmaa, A., Davaabal, B., Zolzaya, Ts., Bayarzul, U., Jadambaa, Ts., Rüscher, C.H.:* Preparation of geopolymer-type mortar and “light-weight concrete” from copper floatation waste and coal combustion by products, Edited by Kriven, W., Wang, J., Zhu, D., Fischer, T., Kirihara, S., *Developments in Strategic Ceramic Materials: Book Series of Ceramic Engineering and Science Proceedings*, Wiley, ISBN: 978-1-119-21173-0, 2015, Volume: 36, Issue: 8, 89-102

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Диспергирование наноразмерного диоксида кремния в базовом моторном масле

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Аннотация
В статье приведены результаты экспериментов по диспергированию наноразмерного порошка диоксида кремния в базовом моторном масле. Исследования проводились на ультразвуковой установке (г. Санкт-Петербург). Установка позволяет работать в режиме кавитации на резонансной частоте ≈ 23 кГц. Мощность ультразвуковой установки составляет 630 Вт. Наноразмерный порошок диоксида кремния для опытов был получен путем испарении исходного вещества под воздействием электронного пучка, созданного ускорителем. Полученную добавку исследовали на испытательном стенде в лаборатории ДВС в двигателе Российского производства.
Ключевые слова: наноразмерный порошок; ультразвук; акустическая кавитация; базовое моторное масло; диспергирование

Dispersing the Nanosized Silica in the Base Motor Oil

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Abstract
Yje paper presents the results of experiments on the dispersing the nano-sized silica powder in the base motor oil which have been conducted using ultrasonic installation (St. Petersburg). The installation allows working in a mode of cavitation at a resonant frequency ≈ 23 kHz. The ultrasound power was 630 watts. Nano-sized silica powder for the experiments was obtained by evaporation of the raw material under the the action of the electron beam produced by an electron accelerator. The resulting additive has been investigated on a test bench in the laboratory of the internal combustion engines in the engine of Russian production.
Keywords: nano powder; ultrasound; acoustic cavitation; base motor oil; dispersion

В Бурятском государственном университете в течение ряда лет ведутся исследования по диспергированию наноразмерных порошков в базовом моторном масле. В предыдущих публикациях рассказывалось об исследовании диспергирования наноразмерного порошка меди [1]. На эту тему получены патенты на изобретения [2, 3]. В одном из исследованием наряду с наноразмерным порошком меди был опробован порошок диоксида кремния. После испытания металлических пластин на машине трения с присадками в моторном масле, образцы были исследованы с помощью сканирующего микроскопа, расположенного в центре общего пользования Восточно-Сибирского государственного университета технологии и управления. На образце, который испытывался с использованием присадки, содержащей диспергированный порошок диоксида кремния, его следы были найдены в качестве наполнителя в кавернах на поверхности металла (см. рис. 1 и табл.1). Эти предварительные исследования показали, что наноразмерный диоксид кремния улучшает условия трения и предохраняет трущиеся поверхности.