

*Bondar V., DSc, Professor
Akhmednabiyev R.M., Associate Professor
Akhmednabiyev R.R., post-graduate
Poltava National Technical Yuri Kondratyuk University*

INFLUENCE OF FLY ASH AND SLAGS OF BOILER WITH CIRCULATING FLUIDIZED BED ON PROPERTIES OF CONCRETE

The properties of fly ash and slag of boilers with circulating fluidized bed are under consideration. In the Donetsk region several new generations of boilers are operating, permitting to burn the poor fossil fuels, including coal tailings. The ash and slag produced in this case are having somewhat different properties in contrast to the conventional waste TPP.

In the study of fly ash and slag's properties, the up-to-date methods are applied, based on X-ray phase (XRD), DT and spectral analyses.

The question of the allocation of a large area of land for the storage of waste at thermal power plants. It was found that in windy weather wastes soar into the air, creating a cloud of dust and chemicals dissolved in rainwater and contaminate groundwater

The aim of the present study is to identify the influence of fly ash on the strength properties of heavy concrete and on its resistance to water saturation and drying.

The research strength of concrete based on mathematical experiment planning

Keywords: *Fly ash, ash and slag, boilers with a circulating fluidized bed, strength, concrete.*

*Бондар В.О., д.т.н., професор
Ахмеднабієв Р. М., к.т.н., доцент
Ахмеднабієв Р.Р., аспірант*

Полтавський національний технічний університет імені Юрія Кондратюка

ВПЛИВ ЗОЛИ-ВИНЕСЕННЯ ТА ЗОЛОШЛАКІВ КОТЛІВ ІЗ ЦИРКУЛЯЦІЙНИМ КИПЛЯЧИМ ШАРОМ НА ВЛАСТИВОСТІ БЕТОНУ

Досліджено властивості золи-винесення та золошлакових мас котлів із циркуляційним киплячим шаром. Зазначено, що у Донецькій області експлуатуються кілька котлів нового покоління, які дозволяють спалювати бідне кам'яне вугілля, в тому числі й відходи збагачення вугілля: золи і шлаки, що утворюються при цьому, мають децю інші властивості, на відміну від традиційних відходів ТЕС. Розглянуто питання виділення значної площі землі під складування відходів на території ТЕС. З'ясовано, що у вітряну погоду відходи здіймаються у повітря, утворюючи хмари пилу, а хімічні сполуки розчиняються у дощовій воді та забруднюють ґрунтові води. Дослідження властивостей зол і золошлаків проведено сучасними методами, заснованими на рентгенофазових (РФА), спектральних та диференційно-термічних аналізах. Виконано дослідження міцності бетонів на основі математичного планування експерименту.

Ключові слова: *зола-винесення, золошлаки, котли із циркуляційним киплячим шаром, міцність при стиску, бетони.*

Introduction: Humanity needs energy, living space, natural and artificial materials, however, these needs, as a rule, cause wastes.

Some wastes are formed in the process of energy production, for example, at burning coal in the heat power stations' boilers. Up to the present moment, at heat power stations of many world countries, coal is burnt in ordinary boilers, which efficiency is rather poor. For the latest 15 – 20 years, there have been produced boilers with a circulating fluidized bed, where coal is being burnt for a longer time than in traditional ones, therefore coal is burnt completely. The similar boilers have been operated in Ukraine since 2001 at one of the largest heat power stations in Europe – Starobeshivska HPS.

Latest study sources and publications review. Ashes and slags are divided into high-calcium ($\text{CaO} > 20\%$ wt) and low-calcium ($\text{CaO} < 20\%$ wt). The first category contains mostly crystalline slag, and the other one – glass and amorphous clay intrusions. High-calcium ashes are divided into low-sulfate ($\text{SO}_3 < 5\%$ wt), obtained at coal and turfs burning, and sulfate ($\text{SO}_3 > 5\%$ wt), obtained at burning slags [2].

There exists no unified classification of ash-slugs wastes. The first classification was made in 1953 at development of the ASTM Standard. In 1960 it was suggested to consider ashes as a pozzolanic admixture, and in 1968 natural pozzolans and ashes were combined into the common ASTM C 618 Standard with a generic name of “mineral admixtures” [3].

Fly ashes do not require any further processing being added to Portland cement or concrete. It must answer the standards requirements [1].

At manufacture of heavy-weight concrete, precast and cast (solid) concrete structures, fly ashes can replace part of sand or cement or it can be used as a separate component: active micro-filler. Slags and ash-slugs can replace sand partly or completely. At using ashes, the properties of concrete improve. Therefore, ashes have acquired a wide application and are very popular among manufacturers.

Fly-ashes and ash-slugs are normally colored in grey or light grey, close to the cement's colour, and ashes and ash-slugs, obtained after coal burning in boilers with a circulating fluidized bed, possess reddish colour tinge. This colouring is determined by transformation of ferric oxide in clay minerals at coal burning, resulting in the terracotta colour.

Products of Portland cement minerals hydration (C-S-H, hydrosilicates, ettringite, etc.) in the cement paste are calculated by means of the stoichiometric model, suggested in J.Ronald's paper [5]. Another two clinker phases (aluminates and ferrites) react with water, too, and formulate hydration products in the form of calcium hydro-aluminates and calcium hydro-ferroaluminates. As a result of aluminate's reaction with gypsum, ettringite is formed in cement paste. Later it transforms into monosulfate as a result of its reaction with carbon dioxide.

The degree of clinker materials hydration with slags depends upon many factors, such as W/C (water-cement) ratio, temperature, slag's reactive capacity and fineness of cement components, therefore, it is difficult to predict it. To model slag hydration with clinker minerals it is necessary to mix cement with various amounts of slag and study it at certain age [7].

Problem statement. The assignment of the present paper is studying the properties of fly-ashes and ash slags of boilers with a circulating fluidized bed and their influence on the concrete strength properties.

Basic materials and results. The true density of fly-ash and ash slags was determined by the traditional method, it equals $2,47\text{ g/cm}^3$. The bulk density of fly-ashes makes 800 kg/m^3 , and that of ash slags – 1320 kg/m^3 . Analysis of the ash slags granulometric composition answers the fineness modulus requirements: $M_f = 1,1$. The fly-ash granulometric composition was studied by means of the laser particle analyzer Cilas 990 and it made $0,2 - 500\mu\text{m}$. Fly-ashes mostly contain particles sizing less than $82\mu\text{m}$.

For the more detailed study of fly-ashes and ash slags properties the technology of X-ray diffraction analysis (XRD), spectroscopy and differential thermal analysis (DTA) were used.

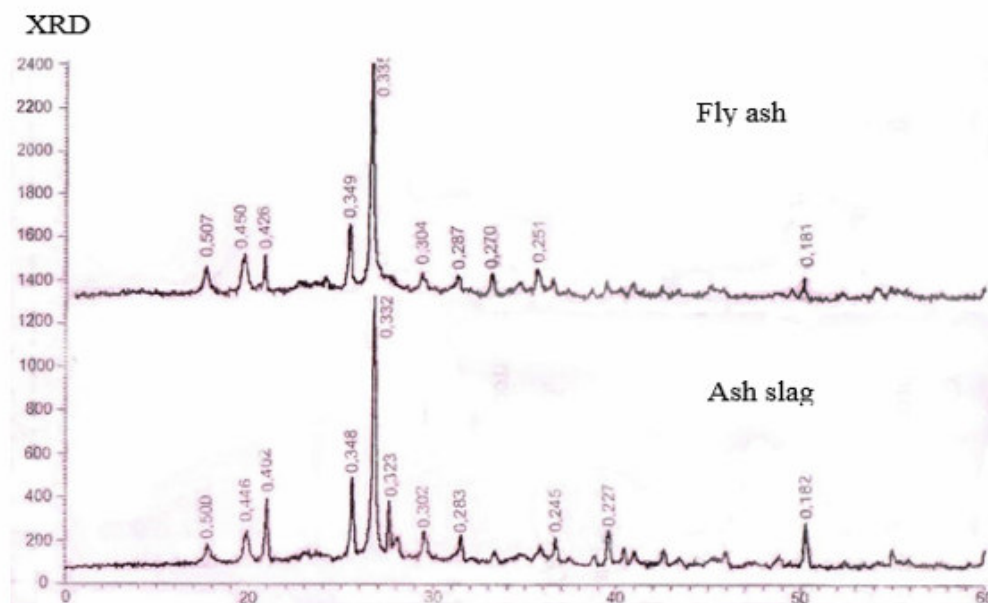


Figure 1 – X-ray diffraction pattern of fly ash and ash slag

Table 1 – Chemical composition of fly-ash and ash slag of boilers with a circulating fluidized bed at Starobeshivska HPS

Composition	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	FeO	ZnO	In ₂ O ₃
Fly-ash	26,89	48,95	7,36	3,90	5,17	0,81	6,12	0,04	0,76
Ash slag	5,03	16,07	5,32	1,62	68,64	0	3,32	0	0

As to the amount of CaO, fly-ash belongs to low-calcium (CaO <20 % wt), i.e. to acidic ashes; as to the content of SO₃ - to sulfate (SO₃ > 5 % wt) ashes. Ash slags belong to high-calcium (CaO > 20 % wt), i.e. to basic ashes; as to as to the content of SO₃ - to sulfate (SO₃ > 5 % wt) ashes.

As it is shown in Table 1, fly-ash and ash slag do not contain the unburnt coal part, thus eliminating restrictions for their application in heavy weight concretes. The most detrimental component is sulfur gas which can be combined with other oxides as anhydride CaSO₄ or ferrous sulfate FeSO₄. In the both cases, sulfur compounds can induce delayed ettringite formation, which can cause destruction of the set cement structure.

In the course of the present research the influence of fly-ash on heavy weight concretes' water saturation and drying resistance was studied. The mathematical experiment planning method was applied for the study. The following factors were considered variables: X₁ – cement content; X₂ – fly-ash content, which varied from 0 to 1; X₃ – content of superplasticizer «Fluid Premia 196» based on modified polycarboxylates. The study was performed on the test cubes with the edge length of 100 mm. To manufacture the test cubes, small fraction granite crushed stones of 5 – 10 mm, gravel sand with the fineness modulus M_f = 1.1, mark 500 cement of Balakliya plant, Kharkov region, and fly-ash of boilers with a circulating fluidized bed were applied. The samples were manufactured in the metal forms and stored in the laboratory conditions for the 28 days period.

After setting, the basic samples were tested for strength at compression. The results of the test were processed by the «STATISTICS – 10» program and are presented in Fig. 2.

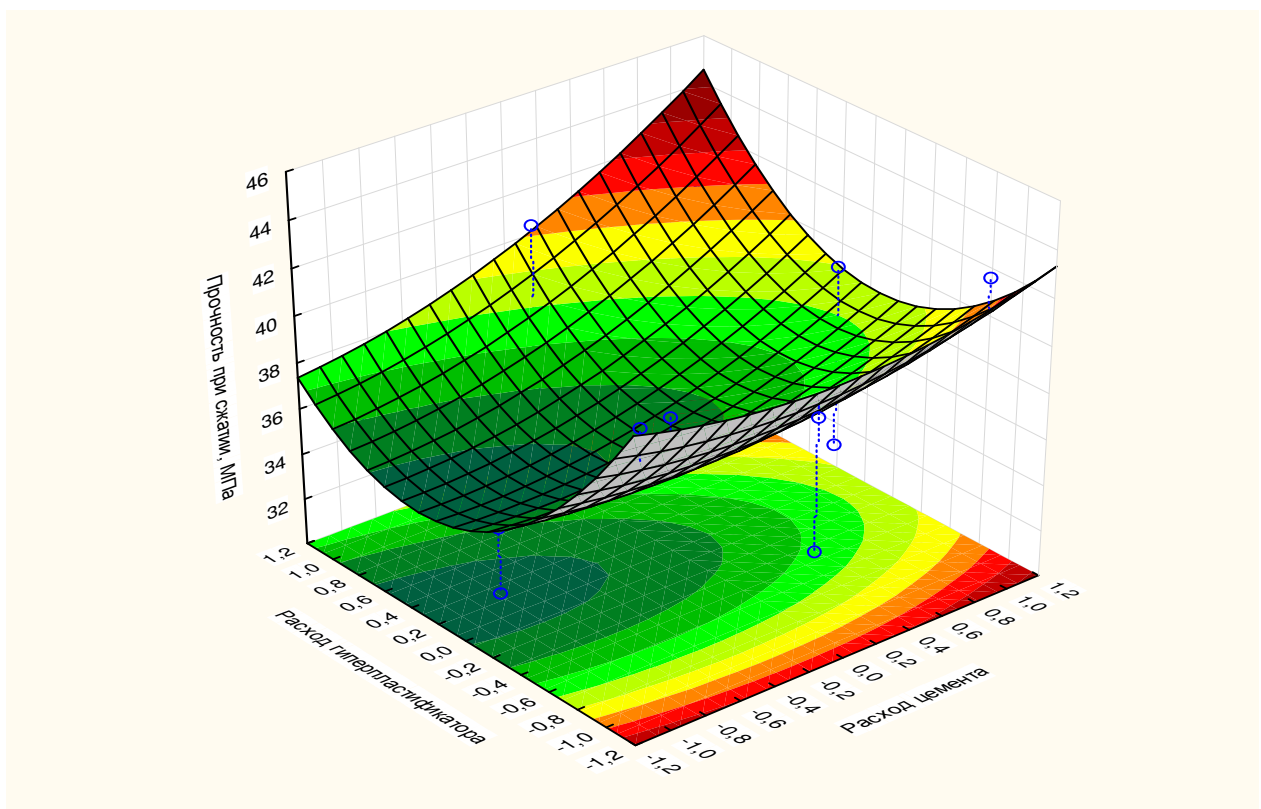
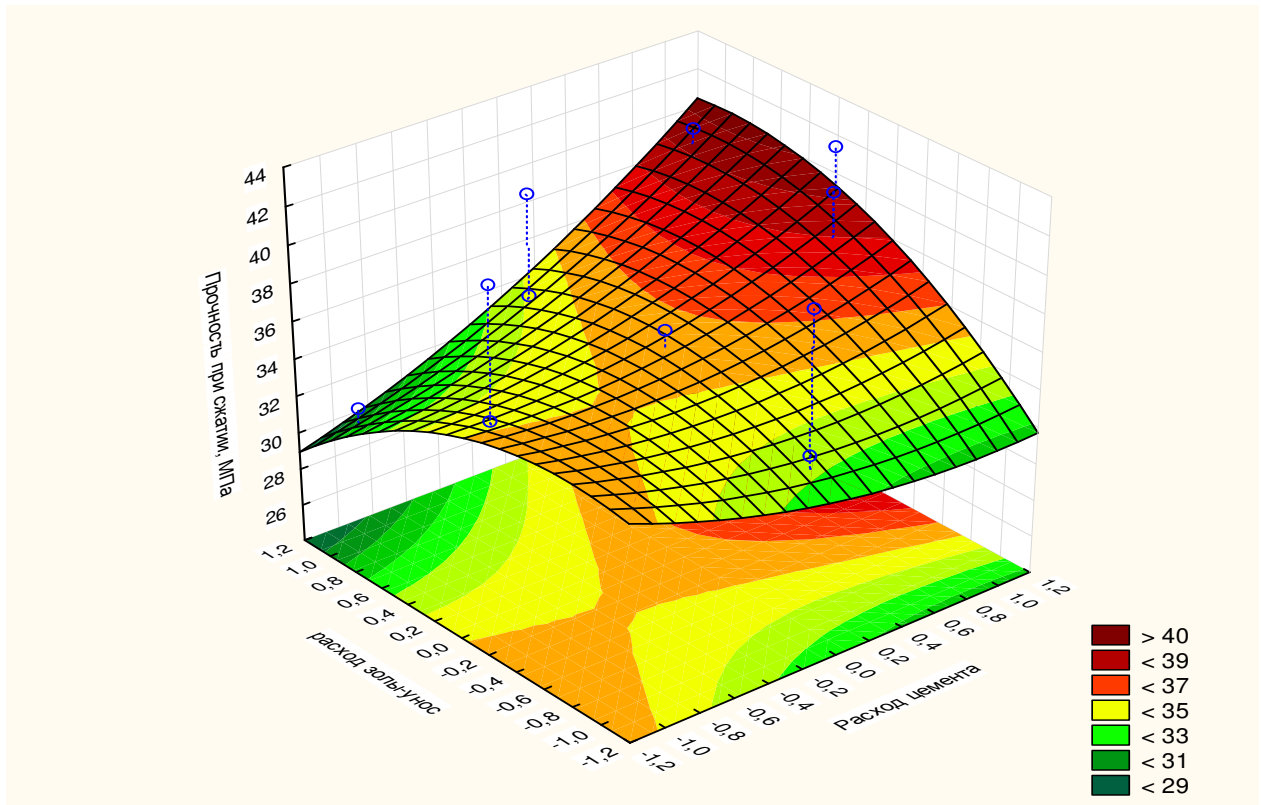


Figure 2 – Surfaces of the variable parameters influence on strength at compression

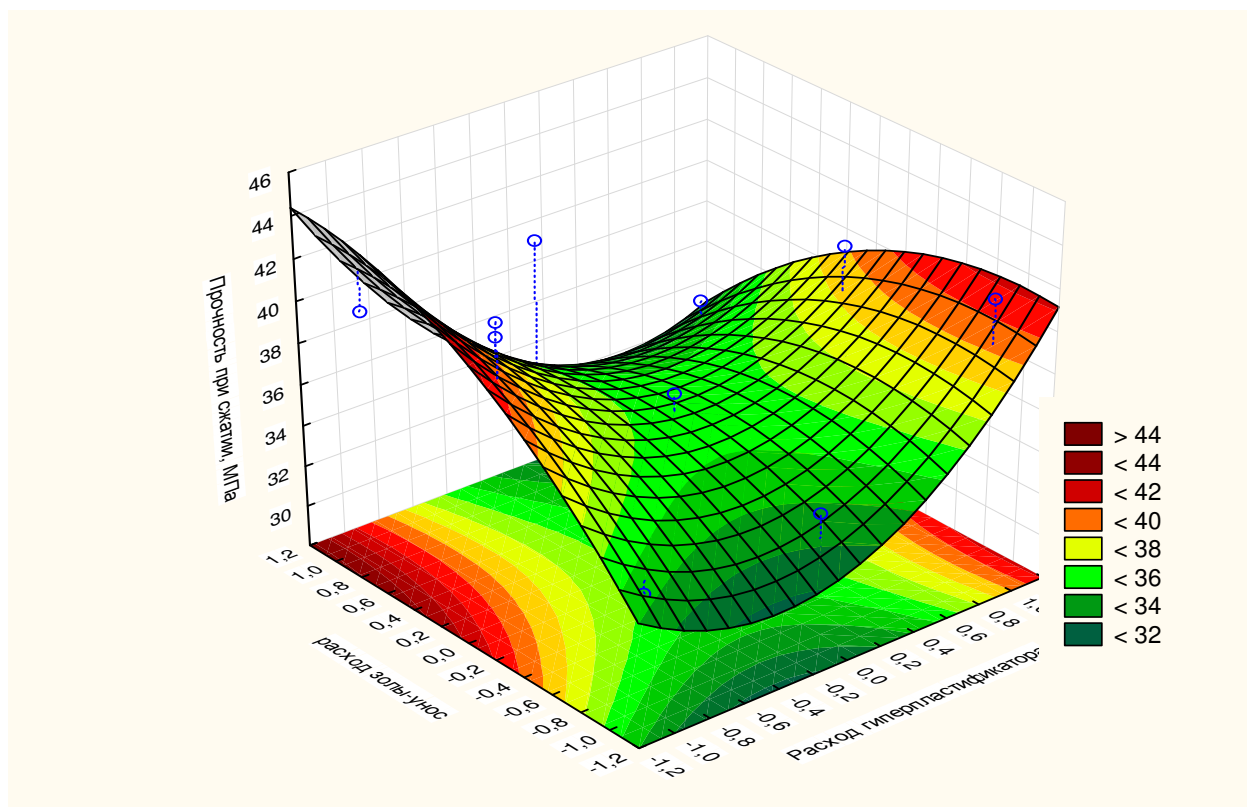


Figure 2 (continued) – Surfaces of the variable parameters influence on strength at compression

Three series of samples, where the fly-ash part was of the maximum, minimum and medium value, were tested for water saturation and drying resistance. The basic samples were submerged into water for the 24 hours period, and the control ones remained stored in the laboratory. Then the samples were drawn out of the water, dried during the 24 hours period at the temperature of 110 °C. After 50 cycles they were tested for strength at compression. The test results are presented in Fig. 3.

The diagrams demonstrate that with increase of the cement content the concrete strength grows at compression, just as it was expected. However, the influence of fly-ash on the concrete strength at compression is different. Thus, at the minimum and maximum values of fly-ash content, the concrete strength at compression is lower, and at the medium fly-ash content values the concrete strength at compression insufficiently grows. Obviously, at the medium values, concrete acquires the maximum consolidation, due to which concrete strength at compression grows.

The presence of plasticizer contributes to the concrete strength growth at compression. With increase of the plasticizer content within the experiment, the concrete strength at compression is ratably growing. At analyzing the common influence of the fly-ash and plasticizer content, one can allocate the range of their best content (the medium fly-ash and plasticizer content) which makes 1.0% of the cement weight.

The diagram shows that after testing for water saturation and drying resistance the basic samples demonstrated reduction of strength at compression by 4,5 – 11,5%. It must be noted that concrete acquires high density at using fly-ash, which contributes to lower water saturation.

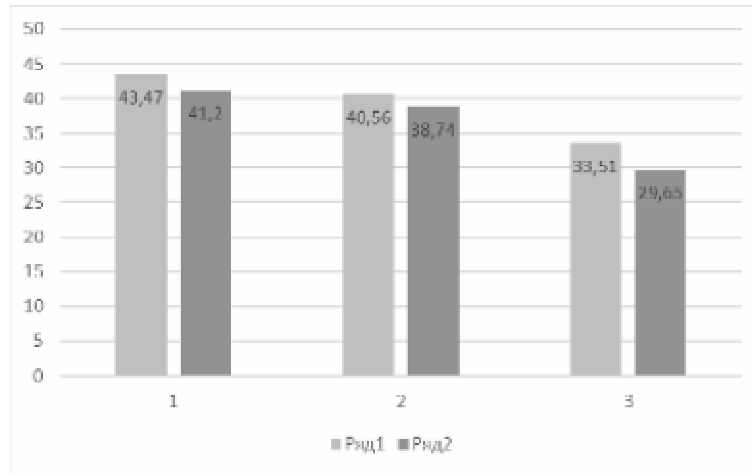


Figure 3 – Comparative analysis of strength at heavy weight concretes compression after 50 cycles of moisturizing and drying:

1 – fly-ash free samples; 2 – samples containing ash and sand 1:1;

3 – samples where sand is completely replaced with fly-ash.

Column 1 – control samples; Column 2 – basic samples

Thus, it was determined that heavy weight concrete strength reduced by 23% with sand completely replaced with fly-ash at the age of three months. Obviously, at the above age, microsilica suspension is still inert to the Portland cement hydration products.

Some ashes and ash slag oxides are known to react with Portland cement clinker minerals or with their hydration products [7]. Portland cement acquires strength at setting mainly due to calcium silicates (C_3S i C_2S) hydration. Hydration results in the formation of calcium silicate hydrates of the C-S-H type and calcium hydroxide CH. The latter is able to react with silicon oxide, contained in ashes and ash-slags of heat power stations, and to form low-basic calcium silicate hydrates [5].

Thus, the more ashes and ash slags of silicon oxide are in the amorphous state, the more low-basic calcium silicate hydrates are formed. However, the above reaction is running slowly at ordinary temperatures, and before reaching the brand age of concrete setting, ashes and ash slags remain in concrete as an inert filler [7]. This fact can explain reduction of concrete strength in the diagrams.

Superplasticizer «Fluid Premia 196» helps to concrete strength increase at compression, and its best content makes 1.0 – 1.2% of the cement weight. The similar effect is described in V. M. Malhotra's article [4].

When sand is replaced with fly-ash of boilers with a circulating fluidized bed, heavy weight concretes' water saturation and drying resistance does not reduce [6]. In the course of the experiment no cracks in the samples was found, thus testifying to the absence of the internal stress. It is fair to assume that mineral ettringite had already been formed in the process of concrete setting, however, this hypothesis requires further verification by the respective research.

Conclusions. It was determined that ashes and ash slags of boilers with a circulating fluidized bed do not contain unburnt coal particles. As to their chemical composition, it is similar to that of clay, however, they have a high water demand. Concrete strength, when sand is replaced with fly-ash, is reducing at the initial setting terms, though the concrete density is growing. Concrete water resistance does not reduce with introducing of ashes and ash slags if compared to traditional sand.

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Received 10.05.2016