Investigations of physicochemical properties of dusts generated in mechanical reclamation process of spent moulding sands with alkaline resins

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Abstract: Mechanical reclamation processes of spent moulding sands generate large amounts of post-reclamation dusts mainly containing rubbed spent binding agents and quartz dusts. The amount of post-reclamation dusts, depending in the reclamation system efficiency and the reclaim dedusting system, can reach 5%–10% in relation to the total reclaimed spent moulding sand. The proper utilization of such material is a big problem facing foundries these days. This study presents the results of investigations of physicochemical properties of post- reclamation dusts. All tested dusts originated from various Polish cast steel plants applying the mechanical reclamation process of moulding sands with alkaline resins, obtained from different producers. Different dusts, delivered from foundries, were tested to determine their chemical composition, granular characterization, physicochemical and energetic properties. Presented results confirmed assumptions that it is possible to utilize dusts generated during mechanical reclamation of used sands with organic resins as a source of energy.

Key words: dust; recycling; environmental protection; reclamation; moulding and core sands; energy
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Sand casting is one of the most common and most widely used method of casting which involves the pouring of molten metal into a mould including typically silica sand, clay binders (mostly bentonite), water or a variety of organic or inorganic chemical binders. In a group of chemical bonded sands, the moulding sands with furfuryl resins applied in a foundry practice have presently the highest share of the castings production out of technologies using no-bake, self-hardening sands, in which quartz matrix is bound by chemisetting binding agents [1-3].

The quality of castings produced in such moulding sands is high, and the technology is universal, to a considerable degree, both in respect to the applied casting alloy (cast steel, cast iron) and in respect to the size and complexity of the castings.

The necessity of rational waste sands management and introduction of environment friendly chemically hardened binders are the factors determining a further development of the self-setting sands technology. In the first case, a universally applied reclamation admittedly allowed the limitation of the amount of spent sands requiring management, but on the other hand, emphasized the need to utilize significant amounts of post-reclamation dusts, characterised by an increased concentration of harmful substances. Dusts generated in the mechanical reclamation process are often "hazardous waste" due to a significant content of organic substances.

Considering the global annual production of castings being approximately 100 millions of metric tons, the scale of the management problem of waste sands and post-reclamation dusts is the subject of several regulations and acts, at both the national and international levels.

The high cost of new silica sand and the growing cost of disposal of used foundry sand, make the reclamation and re-use of sands a matter of increasing importance to reduce the quantity of sand that must be disposed of at waste sites [3-5].

Two types of reclamation are commonly used, mechanical attrition and thermal. The most commonly practiced method because of its lowest cost is mechanical. Mechanical attrition partially removes the residual binder from sand. Whatever method of reclamation is used, there is always some loss of sand so that 100% reclamation can never be achieved. Sand losses include: burn-on, spillage, inefficiencies in the sand system and the need to remove fine particles. Dust losses of around 5% can be expected and total sand losses of up to 10% may be expected. Binder systems containing inorganic chemicals (e.g. silicate based systems), alkaline phenolic resins (containing potassium) or binder system containing phosphoric acid are difficult to reclaim at high percentages because no burn-on of the inorganic material occurs.

Increasing requirements concerning the reclaimed material quality (small ignition losses and dusts content in the matrix below 0.5%) constitute factors causing the necessity of a more efficient matrix purification. This is usually done by an intensification of physical means applied for a dry removal of spent binders (grinding, rubbing, crushing, pneumatic classification), however such procedures increase amounts of dusts generated after reclamation [6-8].

Regulations by law of the European Union drastically limit the free furfuryl alcohol content, classified as a toxic product, to a level below 25% as well as elimination of dangerous **B**(enzene),**T**(toluene), **E**(thylbenzene), **X**(ylene) and **P**(olycyclic), **A**(romatic), **H**(ydrocarbons) gases emitted during foundry processes.

As a result of restrictions, the producers of binding agents for moulding sands are obliged to search for new binders that are more environment- and employee-friendly.

To this group belong, among others, binders used in the ALPHASET technology (the technology of self-hardening mixtures phenol resin – ester is based on the two-component binding system, where the alkali phenol resin is the binding component). These binders are of a basic character.

Spent foundry sands with alkaline resins can be reclaimed by the mechanical methods, allowing efficient recycling process of the quartz matrix, in which a significant amount of fresh high-silica sands can be substituted by the reclaimed material with a simultaneous decreasing of the resin addition to the newly prepared moulding sand [9-11].

One of the main criteria of assessing the obtained reclaim quality in systems of multiple circulations of a matrix, which decides on its qualifying as the fresh sand substitute at preparing moulding sands, is the reclaim ignition loss, which should be below 3%. In case of insufficient removal of spent binders from surfaces of matrix grains, the moulding sand has a high gas evolution rate and increased N (nitrogen) and S (sulphur) content in the matrix (which should not exceed 0.15%). The nitrogen content in a matrix can be the reason of defects in iron and steel castings, while the sulphur content above 0.15% can cause a flake graphite occurrence on surfaces of iron castings with nodular graphite [12, 13].

1 Physicochemical properties of dusts generated in mechanical reclamation of used moulding sands with alkaline resins

The present investigations were conducted in the Faculty of Foundry Engineering, AGH University of Science and Technology within the project entitled "Elaboration of innovative technology of after reclamation dusts thermal utilization - in an aspect of waste heat recovery" [7].

The investigated dusts originated from various foundry plants, applying moulding sands with alkyd and resol type resins. These binders are characterised by different properties according to the used resins, mechanical reclamation systems, spent sands overheating degree (kind of casting material — cast iron or cast steel, casting size) and the efficiency of the dedusting system of the reclaimed materials operating in individual foundry plants.

Aimed at the development of the utilisation method of post-reclamation dusts generated in the dry reclamation process of moulding sands with alkaline resins, the following basic physical and chemical properties of post-reclamation dusts were tested:

- ♦ Chemical composition and properties
- ♦ Grain size, physical density of dusts, gas evolution rates
- ♦ Loss on ignition
- ♦ Elution
- ♦ Energetic properties

1.1 Dusts with alkaline resin residues applied in investigations

The results of investigations of physicochemical properties referring to seven kinds of post-reclamation dusts are presented. All tested dusts originated from various Polish foundry (cast steel) plants applying the mechanical reclamation process. These dusts are marked as follows:

P3: post-reclamation dust obtained from used moulding sand of the initial composition: matrix (40% of fresh high-silica sands and 60% of a reclaim). As a binder in sand composition the phenolic binder (Permabind 44, producer Eurotek England) with ester hardener (Permabind 132) is applied. Steel castings of a mass up to 12 metric tons were produced in the moulds prepared with this moulding sand. The spent moulding sand reclamation process was performed in the vibratory crusher and column reclaimer (of the IMF Company) with a yield of 15 – 20 metric tons per hour. Dusts were submitted for the utilisation by the special unit.

P7: dust obtained from spent moulding sand (resin SL2002, hardener Katalizator KL, producer PRECODLEW Poland) containing, as its matrix, high-silica sand and chromite sand (in proportion 5.7:1 respectively), which in the reclamation process was subjected to magnetic separation. Steel castings of a mass up to 75 metric tons were produced in moulding sand with alkyd binder. The reclamation process was performed by the mechanical method in the GUT reclaimer. The reclaim properties: ignition losses approx. 2.5%, pH = 8, dust fraction content < 0.5%. Dusts amounts in a year of approximately 1,500–1,800 metric tons, post-reclamation dusts were handed over to an external company.

P10: post-reclamation dust obtained from used moulding sand (resin Avenol 700 NB, hardener Katalysator 4040 – producer ASK Chemicals) of the initial composition: matrix (40% of fresh high-silica sands and 60% of a reclaim). As a binder in sand composition, the resin from ALPHASET technology

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was applied. Iron and steel castings of a mass up to 500 kg were produced. The spent moulding sand reclamation process was performed in a mechanical system of the EUROTEK (TROJAN) Company. Dusts gathered for a year in the amount of approximately 50 metric tons were stored at the foundry and then handed over to the outlined part of the waste stockpile. The reclaim properties: ignition losses approx.1.0% –1.5%, pH = 7.2–8.8, powdery fraction content up to 1.0%.

P11: dust obtained from spent moulding sand (resin SINOTHERM 8426, hardener AKTIVATOR J340 – producer Huttenes Albertus) containing, as its matrix, high-silica sand and chromite sand (in proportion 30:1), which in the reclamation process was subjected to magnetic separation. Steel castings of a mass up to 20 metric tons were produced in the moulding sand in which, as a binder in sand composition, the resin from ALPHASET technology was applied. In foundry the mechanical reclamation of the GUT Company was typically applied. However, on account of a low reclaiming ability of spent moulding sands from the ALPHASET technology, additional tests aimed at the reclamation improvement were performed. The new type of vibratory reclaimer, integrated with the cascade air classifier, called REGMAS [11], developed in the Faculty of Foundry Engineering AGH, University of Science and Technology, by the authors of this paper, was applied [14]. In order to obtain dust P11 the spent moulding sand was reclaimed in one cycle of the reclamation treatment.

P13, P14, P15: three additional post-reclamation dusts, obtained from the same spent moulding sand as dust P11, by means of the reclamation, at the following conditions of the reclamation treatment in the vibratory device REGMAS [14]:

These additional dusts are marked as follows:

P13 – dust generated during the I-st reclamation cycle;

P14 – dust generated during the II-nd reclamation cycle;

P15 – dust generated during the III-rd reclamation cycle.

The universal vibratory reclaimer REGMAS, functionally integrated with the pneumatic cascade classifier, is used to the dry mechanical reclamation of practically each used sand. It can be installed in reclamation seats of small and middle size foundry plants. The view of the unit with the cascade classifier, without the external screen is shown in Fig. 1.

Used sands, after the separation of metallic contaminations, are supplied to the device charge. The primary reclamation is realised on the crushing grid and on the set of 3 sieves. The lowest sieve is of a conical shape of clearances between vertical elements of palisade (slits) being 1.25 mm. At the bottom of the reclaimer, in its buffer part, loose metallic abrasive elements (spheres) are placed. Together with the vibratory influence they realise the secondary reclamation. The sand screened via the conical sieve is transferred by the vibratory trough and proportioning system into the cascade classifier, supplied from the bottom by a controlled air speed fan. The reclaimer is set in motion by means of two rotodynamic motors of a controlled rotational speed and a set vibration agitation force.

Fig. 1: View of experimental REGMAS reclaimer

1.2 Physicochemical properties of post-reclamation dusts

To assess the possibility of storage or management of post-reclamation dusts, it is necessary to determine the basic physicochemical properties of the investigated dusts. The basic physicochemical properties of the investigated post-reclamation dusts from moulding sands with alkaline resins are listed in Table 1.

The chemical compositions of the investigated post-reclamation dusts from the moulding sands with alkaline resins are given in Table 2, while results of granulometric analysis of dusts performed by the laser diffraction method by means of the Analysette 22 NanoTec apparatus (of the FRITSCH Company) are presented in Table 3.

Table 1: Basic physicochemical properties of investigated post-reclamation dusts from moulding sands with alkaline resins

Determined properties of dust	Marking of post-reclamation dust						
	P3	P7	P10	P11	P13	P14	P15
Mass density (average value), $g{\cdot}cm^{-3}$	2,50	1,59	2,57	2,52	2,36	2,42	2,59
pH value	10.2	9.01	10.41	10.82	7.85	7.64	7.99
Moisture, % by mass	1.30	1.15	2.26	0.70	1.90	2.00	0.90
Electrolytic conductivity, mS	7.35	0.84	6.24	23.92	12.86	7.59	4.71
Loss on ignition at temp. 950 °C, % by mass	5.50	22,17	3.59	4.38	9.79	8.94	4.42
Emissivity of gases at temp. 1,000 °C in CO_2, $cm^3{\cdot}g^{-1}$ of dust	36	125	21	31	66	53	30
Acid Demand Value, ADV	40.50	24.50	11.73	10.42	10.50	8.00	11.50

Table 2: Chemical compositions of investigated post-reclamation dusts from moulding sand with alkaline resins

Chemical component	Marking of post-reclamation dust, content in % by mass						
	P3	P7	P10	P11	P13	P14	P15
Al_2O_3	13.12	10.03	5.35	9.49	2.20	1.98	1.11
CaO	0.62	0.51	0.89	1.14	0.28	0.31	0.36
Cl	0.014	0.012	0.027	0.030	0.012	0.012	0.010
Fe_2O_3	1.99	3.51	2.16	8.58	0.87	0.96	0.90
K_2O	1.92	0.14	0.32	1.00	0.47	0.45	0.36
MgO	1.70	0.92	0.45	1.26	0.16	0.17	0.16
Na_2O	0.44	0.54	4.31	2.67	1.09	0.92	0.47
SiO_2	71.70	50.80	81.00	64.10	81.80	84.80	87.95
SO_3	0.15	1.12	0.01	0.05	0.05	0.03	0.01
ZrO_2	0.23	2.06	0.46	0.88	0.42	0.38	0.35
LOI (loss on ignition)	5.50	22.17	3.59	4.38	9.79	8.94	4.42
Total	97.38	91.819	98.57	93.52	97.14	98.95	96.09

Table 3: Selected data of size analysis of dusts from reclamation of moulding sands with alkaline resins performed by laser diffraction method by means of Analysette 22 Nano Tec apparatus

Determined size parameter of dust	Marking of post-reclamation dust						
	P3	P7	P10	P11	P13	P14	P15
Arithmetic mean of dust particle diameter, μm	92.56	46.79	31.08	61.49	74,65	77.69	78.87
Specific surface of dust particles, $cm^2{\cdot}g^{-1}$	6037	18998	9143	5671	6272	5662	6776
Homogenity of dust	0.81	0.79	1.71	0.65	0.80	0.71	0.70
Mass fraction of dust particles size of 1,0 – 56,0 μm, % by mass	40.24	35.39	84.94	51.83	47.94	44.58	42.95

Table 4: Results of elution test of selected dust P7 from reclamation of moulding sand with alkaline resin (Test liquid : dry matter = 10 : 1)

Determined parameter of dust	Dust P7 $mg{\cdot}kg^{-1}$ of dry matter	Polish requirements for wastes storage on dump of inert wastes $mg{\cdot}kg^{-1}$ dry matter	Polish requirements for wastes storage on dump of waste different than hazardous and inert $mg{\cdot}kg^{-1}$ dry matter
Sulfates	56.4	1,000	20,000
TOC	709.7	30,000	-
Phenol index	0.18	1	-
Fluorides	26.82	10	150
Chlorides	70.7	800	15,000
Copper	0.13	2	50
Lead	< 0.05	0.5	10
Nickel	0.19	0.4	10
Chromium total	0.053	0.5	10
Zinc	0.41	4	50
Cadmium	0.001	0.04	1
Molybdenum	< 0.1	0.5	10
Antimony	< 0.05	0.06	0.7
Arsenic	< 0.05	0.5	2
Mercury	< 0.005	0.01	0.2
Barium	0.74	20	100
Selenium	0.23	0.1	0.5
BTEX (total)	4.75	6	-
PCB (total)	< 0.35	1	-
Mineral oils	6.5	500	-
PAH (total)	< 0.64	1	-
Dissolved organic carbon (DOC)	471.3	500	800
Total dissolved substances (TDS)	3,890	4,000	60,000

Table 5: Technical analysis and energy properties data of dusts from mechanical reclamation process of moulding sands with alkaline resins

Determined property, symbol, metric unit	Marking of post-reclamation dust						
	P3	P7	P10	P11	P13	P14	P15
Ash content A^a, % by mass	93.9	77.4	96.7	96.7	93.2	93.9	96.3
Volatile matter content V^a, % by mass	3.70	7.82	2.08	2.96	4.85	4.47	2.64
Heat of combustion Q_s^a, MJ·kg^{-1}	1.382	6.769	0.209	0.330	1.518	1.363	1.110
Calorific value Q_i^a, MJ·kg^{-1}	1.304	6.589	0.161	0.290	1.436	1.228	1.047
Total sulphur content S_t^a, % by mass	0.04	0.02	0.01	0.02	0.02	0.02	0.01
Ash sulphur content S_A^a, % by mass	0.04	0.02	0.01	0.02	0.02	0.02	0.01
Combustible sulphur content S_C^a, % by mass	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon content C_t^a, % by mass	4.0	18.4	1.1	1.5	4.2	3.8	2.3
Hydrogen content H_t^a, % by mass	0.29	0.77	0.14	0.15	0.34	0.31	0.17
Nitrogen content N^a, % by mass	0.08	0.77	0.02	0.04	0.07	0.07	0.04

Legend for Table 5:
Ash content A^a — amount of an ash contained in the analytical sample of fuel.
Volatile matter content V^a (analytical state) — amount of a volatile matter contained in the analytical sample of fuel.
Heat of combustion Q_s^a (analytical state) — heat emission during a combustion process.
Calorific value Q_i^a (analytical state) denotes the same heat amount, which evolves during the complete combustion.

In order to assess the possibility of storing post-reclamation dusts in storage yards of the given type, it is necessary to perform the elution test. The test results for selected dust P7 are shown in Table 4. The criteria binding for neutral wastes and for wastes other than dangerous and neutral are also given for comparisons. The more strict the criteria, the higher payments are required for waste storing in the given storage yard.

1.3 Energy characteristics of post-reclamation dusts

Since one of the directions of the management of post-reclamation dusts originated from moulding sands with organic binders is their thermal utilisation, e.g. in the co-burning with carbon carriers process or in individual burning, it is necessary to determine energy properties of these dusts. The results of energy properties data and technical analysis of post-reclamation dusts are presented in Table 5.

2 Discussion of results of dusts investigations

Post-reclamation dusts originating from the mechanical reclamation processes of moulding sands with alkyd resins significantly differ in their physicochemical properties, chemical compositions and energy properties. This is mainly caused by the applied reclamation system and its efficiency, reclaimed material dedusting system efficiency as well as by the efficiency of the mixture separation of high-silica and chromite sands applied as moulding sands matrices.

Dust P7 contains a large amount of carbon (ignition losses above 22%), which causes a high emissivity of gases and a high calorific value at a level of 6.589 MJ·kg^{-1} (for comparison: dust P3 has a calorific value: 1.304 MJ·kg^{-1}). Dust P7 is also characterised by a significantly lower ash content. From the point of view of a suitability of post-reclamation dusts for the energy recovery in the co-burning process with other energy carriers, dust P7 meets the requirements. The lowest calorific value at 0.161 MJ·kg^{-1} indicates dust P10. For comparisons, the basic energetic data of the main energy carriers are given in Table 6.

Differences in properties of both dusts, originated from the reclamation of moulding sands with alkyl resins, can be caused by kinds of castings or by the applied reclamation systems. Admittedly, in both foundry plants, steel castings are made in these moulding sands, but dust P3 originates from the plant where castings are of a mass up to 12 metric tons, while dust P7 comes from the plant producing castings of a mass up to 75 metric tons. Thus, the sand overheating degree in the second case is much higher and the mechanical reclamation process is easier, since it is supported by the heat auto-reclamation due to which the spent binder removal from matrix grains is more effective.

Table 6: Calorific values and elements composition of main energy carriers

Energy carrier	Content, by mass%				Calorific value MJ·kg^{-1}
	Carbon C	Hydrogen H	Oxigen O	Sulphur + Nitrogen S + N,	
Biomass	< 50	6	43	0.3	14 – 19
Peat coal	56 – 62	5 – 6	32 – 38	0.5	21 – 24
Lignite	58 – 78	4.5 – 7.5	10 – 35	0.8 – 4	24 – 31
Anthracite and hard coal	75 – 96	1 – 6	1 – 18	0.8 – 2	32 – 35
Crude oil	~ 89	8.4	2	0.6	~ 47
Natural gas	~ 86	6.5	0,1	0.1	~ 48

Elution tests of post-reclamation dusts with alkyd resins (dust P7 as an example), which are necessary at their storage or management outside foundry practice, indicate that all parameters allowing storage of these dusts on neutral wastes dumping grounds are fulfilled. Performing this type of testing for each dust before undertaking a decision concerning its application, is of course necessary.

Post-reclamation dusts originated from the mechanical reclamation of moulding sands from the ALPHASET technology (P10 and P11) are characterised by a relatively high pH value and a small emissivity of gases. Moreover dust P10 contains much more SiO_2 than dust P11. Results of granulometric analysis presented in Table 3 indicates that dust P10 has a specific surface 60% greater than dust P11, which is the result of a very large content of the finest fraction (< 56 μm) and significantly smaller diameter of dust P10 particles. Both dusts indicate minimal calorific value at a level of 0.161 (dust P10) and 0.290 (dust P11) MJ·kg^{-1}, which indicates they are not suitable for the thermal utilisation.

It is worth noting that the reclamation performed in the vibratory reclaimer REGMAS significantly improves parameters of dusts in a range of calorific values (dusts: P13, P14 and P15). Carbon content in dusts as well as ignition losses increase and in consequence dusts obtain calorimetric values at a level of 1.047 – 1.436 MJ·kg^{-1}. It can be judged that the reclamation and classification processes of the reclaimed matrix while in the reclamation system of the given foundry plant require the proper regulation of the realised processes (reclamation, dust extraction, classification). Ensuing differences of the obtained effects can be partially caused by a small reclaiming ability of moulding sands from the ALPHASET technology.

Taking into account relatively high calorific values of some investigated dusts, it can be assumed that the efficient method of their utilization will be either combustion in the gas stream (for the initiation and later on when needed to sustain burning) or co-burning with solid carbon carriers (e.g. hard coal or brown coal). Within the research Project [7], both these directions of the utilization of post-reclamation dusts originated from the mechanical reclamation of moulding sands with organic binders are realized.

3 Conclusions

(1) All tested dusts are of a minimal chlorine content (0.01 – 0.03%), which warrants that dioxines and furanes will not be generated during their thermal treatment.

(2) All dusts are characterised by a high alkalinity (pH app. 10), in addition to which as the reclamation process intensifies, pH values decrease to nearly neutral (dusts P11, P13, P14 and P15).

(3) The opinion that moulding sands from the ALPHASET technology are very difficult to reclaim by means of the mechanical treatment (ignition loss of dusts, app. 4%, and thus carbon removed from the grain surfaces are very small) is confirmed. Subjecting this sand to the successive reclamation cycles favours a further removal of a binder from grain surfaces, which is shown by increasing ignition losses (up to 10% for dusts P13 and P14).

(4) Dust P10 is characterised by a high content of the finest fraction (approximately 90% of dust in the fraction < 0.56 μm).

(5) Elution tests of post-reclamation dusts from moulding sands with alkyd resin (P7) demonstrate only small excesses of fluoride and selenium concentrations in relation to provisions in force at storing wastes on dumping grounds for neutral wastes (it can be the result of a sand rinsing process etc.).

(6) From the energy recovery possibility point of view, the most economic is dust P7, obtained in the reclamation process of a moulding sand with alkyd resin and of which the calorific value equals almost 7 MJ·kg^{-1}.

(7) All dusts obtained in the reclamation process of moulding sands with alkaline resins do not contain in practice sulphur, which is beneficial in case of their thermal utilisation (no emission of sulphur oxides).

(8) It should be remembered that the dusts, properties can be quite different even when obtained from the same reclamation system and at the application of the same resin. Also, the successive batches of dusts can differ among themselves in their chemical composition (mainly in a carbon and silica content), and thus in their calorific values. This is influenced by several other factors:

◆ Dimensions and mass of castings and kind of foundry alloy (cast iron or cast steel) – different overheating degree of moulding sands and thereby their different reclaiming ability

◆ Kind of applied matrix – fresh sand or in a mixture with a reclaim. Binder components are cumulated in a reclaim and therefore an amount of generated dusts during the successive reclamation cycle will be higher than when only a fresh sand is applied or when the reclaim fraction is small

◆ Effectiveness of the reclaim dedusting system - optimisation of the system in order to limit carrying off silica particles

Therefore, it is necessary to develop a system for the thermal utilisation of these dusts to have the possibility of self-regulation of energetic fuel additions – in dependence on the dust calorific value in the given moment.

(9) Effectiveness of the reclaim dedusting system can be a factor influencing the amount of the generated post-reclamation dusts. However, too intensive of a dedusting can cause an excessive carrying off silica dusts, which will generate increased amounts of dusts but will not increase their calorific values and will not improve the purification of matrix grains from binder coatings, while being the reason of matrix losses. A situation when the dedusting system is effective in removal the finest fraction is the most beneficial, since this fraction contains the majority of spent binders.

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