Promising technologies of coal ash and slag waste recycling

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Abstract. Coal ash and slag waste are the products of coal processing that can be recycled into other useful products, but most part of them is accumulated in dumps which causes several environmental consequences. The paper presents a review of the most promising ways of coal ash and slag waste processing based on patent analytics and scientific literature review. Since the patenting process usually comes before innovation implementation, this approach allows to identify the most promising technologies even if they haven't been implemented yet.

1 Introduction

According to the Ministry of Natural Resources and Environment of Russia, Russian coal-fired power plants produce 22 million tons of coal ash and slag annually, and only 10–15% of the waste gets recycled. Consequently, the accumulated coal ash and slag waste is around 1.5 billion tons currently and steadily grows. The Kemerovo Region, solely, faces formation of more than 2.3 million tons of coal ash and slag every year, while hardly 250 thousand tons of the material experiences recycling in reclamation mostly. Coal ash and slag dumps occupy approximately 30 thousand ha. of land in Russia [1]. The increasing generation of industrial waste at a rate drastically overdoing the production volume growth in the country is one of the critical modern challenges. The incremental accumulation of waste entails the explosion of the environmental, social and economic costs because of extremely low level of recycling. In the meanwhile, coal ash and slag have a unique physicochemical composition and physical states to become an extraordinary resource for the high-tech businesses at a great environmental, social and economic effect [2-5].

Recycling of coal ash and slag can help to preserve environment and save and natural resources, and appreciably reduce production cost while prolonging life cycle of facilities, for instance, roads. The Kuznetsk Coal Basin or Kuzbass already possesses certain experience of coal ash and slag recycling but at enormously lower percentage as compared to dumping. For example, since 2017 the Novokuznetsk power engineers execute a mining area reclamation project at a closed mine in Ordzhonikidze district. The project uses ash and slag from the Kuznetsk CHP Power Plant with a view to preventing landslide and erosion processes on the land being reclaimed. At the Belovo Hydro Power Plant, the

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unique aluminosilicate microspheres are manufactured, which enjoy high demand in various industries both in Russia and abroad. Coal ash and slag waste was used in land reclamation of the abandoned coal ash and slag dumps of two power stations: Tom-Usinsk and Belovo Hydro Power Plants. The reclamation was fruitful on the area of large dimensions. The same reclamation projects are now being developed for the Kemerovo and Novo-Kemerovo Heat Power Plants [6].

At this conjuncture, it is crucial to have objective forward forecasts, especially in the area of science and technology. It is impossible to have a clear understanding of advanced technologies without the forward forecasts. The most popular standard methods of forward forecasting are the patent analytics and scientific literature review. The key data sources are patents, patent claims and non-patent literature. Completeness, objectivity, availability and standardization of data enable applicability of formalized analysis and make it possible to obtain the logical and time-ordered information reflective of in-depth processes and qualitative shifts in science and technology [7].

2 Materials and methods

Within the framework of this research, on the authors' request, the Russian database on patents on the ash and slag waste recycling gave out 68 patents, including 15 that were identified by experts-technologists as the most promising. Furthermore, the scope of the review and analysis embraced more than 2000 scientific publications.

The following methods were used to study the ways of coal ash and slug waste recycling:

- Patent analytics, specifically, full patent texts review.
- Review and analysis of scientific literature sources.

From the patent review, it is concluded that the methods of coal ash and slag recycling can be grouped in two major categories—construction, including road construction (bricks, concrete, roadbed aggregate) and extraction of valuable components (aluminium, iron, titanium, rare and rare earth elements, etc.). In this paper, the patents and scientific publications related to coal ash and slag recycling in construction are reviewed with the emphasis laid on the key advantages of the waste processing methods.

3 Results and Discussion

3.1 Raw mixture fabrication technique in frost-resistant masonry block and cast-in-place wall manufacture

In conversion of coal ash and slag into building materials, specific part is related to the raw mixture fabrication technology for manufacturing frost-resistant masonry blocks and cast-in-place walls [8]. In this technology, coal ash and slag after coal combustion are used as binders after dry cooling and activated hardening using alkaline agents of sodium (NaOH) or kalium (KOH), or carbonates of these metals (Na_2CO_3, K_2CO), or lime (CaO), or mixtures of the agents and two water gypsum. Three components are milled together down to a size less than 250 m2/kg.

An advantage is the high porosity of the ash and slag mixture of coal combustion, which lowers thermal conductivity of products, reduces internal stresses in concrete and decreases its fracturing under low temperatures, and the frost resistance of concrete grows as a result.

The validity of this approach was defined in the study [9] which described corrosion types in concrete and the ways of preventing corrosion using special additives. It was also discussed how to improve the corrosion resistance of heavy concrete by adding cement concrete with active aggregates of the second type. Alongside with the standard components, the article discussed the use of the ash and slag mixture to improve the corrosion resistance of heavy concrete. For another thing, the studies included the frost resistance and water impermeability tests of concrete with addition of coal ash. The tests determined such concrete characteristics with coal ash added as:

- The decreased capacity of concrete to absorb water.
- The lowered damageability of concrete owing to actuation of self-healing.
- The changed specific weights in the water to cement ratio.
- The improved compactness of concrete.

Finally, the use of ash and slag in manufacture of concrete is highly economically and technologically beneficial [9].

The principles of manufacturing composite binders from coal ash and slag mixtures for cement, the methods of introducing a coal ash and slag mix in a binder and the influence of coal ash and slag on the properties of a composite binder are in spotlight in [10]. It is mentioned that mechanical activation by joint milling of ash, slag and cement favourably reduces water consumption in composite binders owing to higher dispersiveness of the ash and slag component in cement, which, in its turn, improves plasticisation of the material.

3.2 Foam silicate production

Another promising technology is production of foam silicate [11]. It is proposed to process waste of lignite combustion to manufacture foam silicate or a filtering material capable to adsorb toxic emissions, or an amorphous stock to produce structural and heat-insulating ceramics.

According to this technology, coal is fed in a furnace via a hole in the furnace roof, with gas flow to the molten zone concurrently with blended coal ash and slag. Oxygen-air blasting intensifies thermal and production processes. Oxygen and air are fed both in the melt directly and above the molten zone for full oxidation of carbon. Then, the blend melts in the reducing environment with pre-bringing the content of silicon and calcium oxides in the feed blend to a mass ratio SiO_2/CaO of 1-2. The bubbling ash and slag blend is melted in Vanyukov's furnace-liquid bath. This furnace has two zones for obtaining a liquid melt and for deep reductive melting of ash and slag waste. The zone of deep reductive melting of ash and slag is created through addition of coal and oxygen-air blasting in bottom layers of the melt. The metallic and silicate constituents of the melt are let out separately. The silicate component is cooled in the mode of thermal shock with production of foam silicate.

The main effect is achieved owing to the two-zone structure of the furnace, which enables foam silicate to be free from unwanted impurities of iron and sulfur. An advantage is recycling of sulfur either by its assimilation in the melt and by incorporation of sulfur in the metallic component and exit gases. The reductive melting in the separated zone creates conditions for uniform spread of silicon carbide in the silicate component, which offers background for the highly porous foam silicate production.

3.3 Manufacture of quality products from coal ash

One more promising approach is processing of waste from the systems of hydraulic ash removal at heat power plants with a view to manufacturing quality products from coal ash [12].

The main result of this technique is that the products manufactured from ash have guaranteed properties and quality, and are usable in construction and in manufacture of building materials within a wide range: mineral additives for cement production, additives and aggregate in production of cement grouts, concrete mixtures and dry pack mortars, mineral powder for production of asphalt mixes, etc. The authors of this technique propose a certain commercial-scale procedure. The basic material is fed in a drier drum equipped with a gas-fired burner to dry the feedstock down to moisture content of 0.5%. Then the dried material is discharged to a warm feeder and is delivered to a distribution bin. In the bin, the material is dosed and fed by a belt feeder to a milling facility composed of a centrifugal mill, a classifier, cyclones and a bag filter. This is a special facility as it executes reactivation of the product (recovery of its active properties) and enables assignment of a quality standard for the final product from ash by setting parameters and mode of milling. Reactivation comprises a mechanical process of applied shock and a chemical process of addition of organic additives in the product during its milling. After milling, the material is settled in the cyclones. The post-cyclone air undergoes additional cleaning in the bag filter. The products of aspiration and milling are united. The end product is discharged from the bin and transported to a silo warehouse for storage and shipment.

This method can help solve the problem connected with elimination of ash dumps at coal-fired power plants and is also an example of a resource-saving technology as it enables economizing natural nonrenewable materials used in construction (sand, limestone, etc.) by replacing them by manmade resources–substituents.

One more challenging way of recycling is pelletization of coal ash and slag waste and production of ash pebble [13]. Ash pebble can replace natural pebble in road building, dam construction and concrete production. Owing to the reduced specific gravity and low-level thermal conductivity of ash pebble, the resultant concrete has a lesser weight and a decreased permeability of heat.

The overview of the evident ways of improving the building and engineering properties of dry ash after solid fuel combustion at heat power plants highlights [14]:

- Palletisation toward simple recycling of fly ash as an equivalent of natural raw materials.
- Reduction of hot substances, which is critical for coals with the feature of low volatile yield in classical flaring.
- Air separation by steam curing of one day-old cement stone with addition of initial ash and ash fractions smaller and larger than 10 μm, which adds strength as compared with ash-free cement.
- Milling, as it is found that ash fineness ratio and curing time has influence on the strength of Portland cement.

Finally, anyway, recycling efficiency depends both on the improvement method and on the useful qualities of ash and slag waste.

3.4 Construction materials fabrication technologies

The method of processing low-calcium coal ash and slag waste from heat power plants, with high content of underburnt coal allows production of commodities usable in

manufacture of building materials and in construction [15]. In this method, fluid ash and slag of hydraulic ash handling is dewatered, first, in circular settling tanks and then, in pressure-type filters down to the residual humidity not more than 30%. After that, dewatered ash and slag go to a feed bin for treated waste. When ash and slag are taken for treatment immediately from damps, they go to a wet mill with addition of water to ensure the humidity of 30% and then, after passing the pressure-type filters, to the feed bin for the treated waste. Solid ash and slag are added with water up to the humidity of 30%. After dewatering, settling and pressing, the separated clarified water is returned to heat power plants, which is efficient water management as against the common water use without recycling. Ash and slag of hydraulic ash handling or from waste dumps, given the moisture content not more than 30%, are mixed with a binder. The binder may be lime or clay rocks, namely, lean and fat clay loam, or liquid glass, or high-calcium ash of heat power plants. Additionally, when coal ash and slag waste contains underburnt coal at the content of 15% by mass, milled coal from the feed bin is added. After that, ash and slag undergo pelletization. Then, coal ash and slag pellets are dried on a drying conveyor, and underburnt coal is removed in roasting of the pellets in boiling bed with burning out of coal down to the residual content of not more than 1% by mass, and with the heat utilization via recuperative heat exchanges at heat power plants or at other users. The produced pellets are cooled in refrigerators and sent to storage in bins, or to milling before recycling in manufacture of building materials.

In this manner, this method ensures: high-quality construction materials production; recycling water supply; processing of coal ash and slag both from dumps and from hydraulic ash removal systems; extra heat generation from burning out of unburnt coal. The range of advanced techniques includes processing of coal ash and slag from heat power plants for construction materials manufacturing [16]. The goal of this technology is large-tonnage recycling of treated ash and slag as active mineral additives to cement, concrete and other materials used in production of building products.

The first stage is thermal treatment of a mixture of melted slag and fly ash in a revolver furnace ensuring distillation and removal of alkalis with exit gases to a system of aspiration for the alkali crystallization. Dust from the aspiration system, together with crystallized alkalis, is stored as a self-contained product for the commercial recycling. The second stage is quenching of the slag melt and fly ash mix by air–water jets. The third stage is drying of treated ash and slag down to the humidity of not more than 1%. The fourth stage is magnetic separation of dry ash and slag. The extracted iron oxides (e.g. Fe_2O_3 and Fe_3O_4) are stored and recycled as self-contained products. The fifth stage is dividing of dry ash and slag into coarse and fine fractions suitable for independent recycling in the commercial-scale manufacture of building materials. The sixth stage is fine dry milling of the coarse fraction of treated slag melt and fly ash mix with addition of hardening activators and crushed carbonate rock siftings in an amount of 1–15% of dry mass of the treated slag melt–fly ash. During joint milling, the milled blend undergoes separation of the pre-set fineness size from middlings which are returned back to milling within a closed loop. The activators of hardening are quicklime or cement clinker, two water gypsum and aluminium sulfate. At the final stage, all resultant components are mixed and sent to storage before shipment.

This method is mainly advantageous for the potential treatment of total slag and fly ash of current production at heat power plants, with manufacture of saleable products in the form of active mineral additives for cement, concrete and other materials in fabrication of building products. Being best studied as against the above-described methods, this technique seems to be highly demanded.

The tests of glass ceramic made of fly ash, slag and broken glass were performed at the Angren Thermal Power Plant. The testing aimed to reveal manufacturability of glass ceramic slabs for the construction purposes and to explore processing methods of slag and fly ash.

An effective method of glass ceramic production appeared to be the powder technology and sintering. The manufactured samples had characteristics of glass while their physical and mechanical properties resembled construction ceramics. So, as compared with the conventional ceramic facing plates, the test slabs had higher wear resistance, durability and resistance to discoloration in sun light [17].

A case-study of the Novocherkassk Heat Power Plant provided process solutions on manufacture of active and energy-efficient thermal insulation material made of cellular glass and coal ash and slag. These solutions make it possible to set physical and mechanical properties of cellular glass (density, porosity, thermal conductivity and limit strengths in bending and compression) by means of varying the ash and slag contents in the glass composition. The best compositions of the sample blends are found for thermal insulation plates and blocks made of cellular glass and for porous aggregates for light concrete and fill insulation [18].

A variant of mechanical activation is validated for the mullite–cordierite ceramic production using natural minerals and ash and slag at Heat Power Plant 4 in Omsk. The melting temperatures found in the tests of the mullite–cordierite composite demonstrated the capacity of the material to sustain the temperatures up to 1700–1720ºC. The compression strength of the mullite–cordierite ceramic added with ash and slag and sintered at a temperature of 1400ºC for 3 hours is two times as high as the compression strength of pure mullite samples manufactured in the same conditions. So, the mullite–cordierite composite added with ash and slag is suitable for wide-range production of refractory materials and ceramics [19].

At Dushanbe Heat Power Plant 2, the usability of ash and slag in manufacture of building materials was tested. The tests proved applicability of slag and fly ash in fabrication of ceramic bricks. The bricks had the highest strength at addition of 6.5% fly ash. When addition of fly ash exceeded 10%, the strength of the bricks dropped. The tests allowed correlating stability of ash and ceramic bricks with composition of fly ash from Plant 2 [20].

Coal ash and slag waste from Ukrainian heat power plants was tested in manufacture of lime–ceramic material usable as a binder and a fuel in loam and lime roasting in production of silicate bricks.

Such lime-ceramic binder (1:1–1:1.5) appreciably decreases compression of silicate bricks, increases their frost resistance and makes the bricks look like facing ceramic bricks. Moreover, it becomes unnecessary to mill quartz sand and use ensilage. Furthermore, it is possible to shorten the period of autoclave curing. In this manner, silicate bricks with the lime–ceramic binder possess higher quality geometry and can compete with facing ceramic bricks [21].

The separate research was undertaken to test manufacturability of foamed glass using ash and slag from heat power plants together with broken glass and quartzite sand. The physical and mechanical parameters of the resultant material allow it to replace constructional bricks. Aside from that, the produced foamed glass has better heat insulation properties owing to the porosity and can resist heat transmission in walling of buildings and structures and maintain heat shielding in pipeline and in many other industries and equipment [22].

4 Conclusions

The review of the patent information has reviled the main trends of processing coal ash and slag waste. The recovery of valuable components from the coal ash and slag waste, though requires the new product market exploration, can be the first engineering stage of coal ash and slag waste management toward shaping a high-tech sector of economy in coal mining regions.

As the second stage, it may be possible to use treated waste in construction. This will allow to reduce the size of occupied by ash dumps land, mitigate the environmental impact of dumping and lessen consumption of natural resources.

It is expedient to create interactive regional maps of coal ash and slag waste as a part of a digital platform. Such maps may be sarting points for promising projects on coal ash and slag recycling and also for shaping high-tech sectors of regional economy based on advanced technologies revelation.

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