Characteristic Studies of Yttrium Extracted from Coal Ash, South Korea

Thenepalli Thriveni, Yujin Jegal, and Ji Whan Ahn*

***Abstract*—** The occurrence of Yttrium in the coals with different rankings from their origin was investigated. The concentrations of the rare-earth elements (REEs) in the coal lower than coal ash. Yttrium plays a key role in many industrial applications, defense (targeting and weapon systems, communication, defense electronic warfare) and military (RE permanent magnet (REPM) in flight control motors, Y based ceramics to protect jet engine applications. These rare earths are essential to the success of green technologies. Here we reported the basic characteristics of rare earth elements presented in colas and coal ash samples collected from various coal power plants, South Korea. According to the analysis of coal ash samples Yttrium has higher quantity compared to other rare earth elements presented in coal ash samples. We attempted the extraction of yttrium from coal ash samples by solvent extraction using PC 88 A extractant.

***Keywords*—**Coal Ash, Rare Earth Elements, Yttrium, Coal Power Plants

I. Introduction

THE rare earths or rare-earth elements (REEs) are a group of 17 chemically similar metallic elements (15 lanthanides, including scandium and yttrium). Rare earth elements play an important role in many industrial, petroleum refining, clean energy, automobile, electronics etc. applications and in the military also, widely used for precision-guided munitions, communication systems, lasers, radar systems, avionics, night vision equipment and satellites. These rare earths are highly demanded and essential to the success of green technologies [1]. (Fig.1). Figure.2 shows global demand and consumption of yttrium in phosphors.

Yttrium demand is growing in phosphors used in fluorescent lamps and increasing use as LCD backlights. Beyond 2017/2018 rates of growth may depend on the extent to which LED lamps replace fluorescent lamps. In Europe a system for recycling fluorescent lamps has been in place for some time-but until 2012, rare earths were not recovered.

U.S. Department of Energy (DOE) 2010-2011 Critical Materials Strategy reports includes criticality assessments, and technology analyses to address critical materials challenges. Five rare earth elements (REEs)—***dysprosium, terbium, europium, neodymium and yttrium***—were found to be critical in the short term (present–2015)[2]. DOE's strategy of critical materials research and development (R&D) plans three ways: 1.Diversifying supply 2.Developing substitutes and 3. Improving recycling.

Fig. 1 Rare Earths Applications in Green Technologies

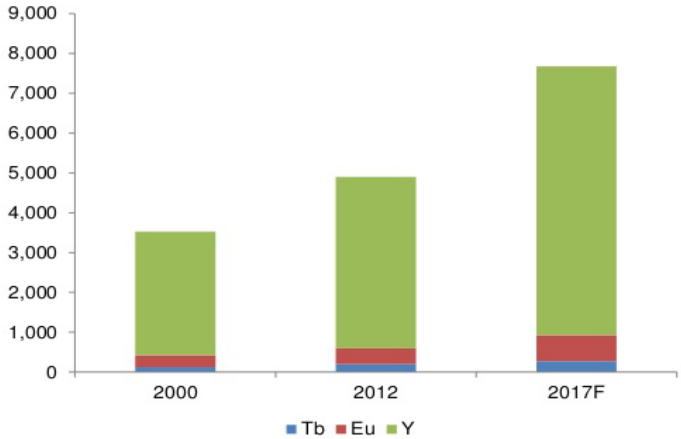

Fig. 2 Yttrium estimated consumption in phosphors 2000-2017F, (t REO)

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II. Rare Earth Applications and Status of US, South Korea

A. The applications of Rare Earth

The applications of rare earths are prominent in green technological areas. The use of REEs to combat global warming and improve energy efficiency has attracted significant attention. The use of several REEs in petroleum fluid cracking catalysts and automotive pollution control catalysts is well known. REE used in magnets reduces the weight of many pieces of equipment such as automobiles. Some REEs are used in in the reduction of carbon dioxide emissions, and have attracted noteworthy attention from public and governmental authorities.

B. Status of USA in Rare Earths Applications

According to the USGS survey, U.S. demand for rare earth elements are also projected to rise as per world demand continues to climb. Demand increases are also expected for rare earths in flat panel displays, hybrid vehicle engines, and defense from cruise missiles to missile guidance systems, smart bombs, night-vision technology and medical applications. The 2015 composition of U.S. and world demand is shown in Fig. 3[3].

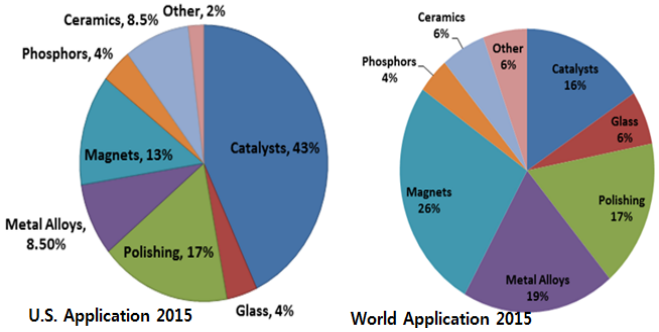

Fig. 3 Rare earth metals demand by application U.S and World, 2015

C. South Korea

South Korea has lack of rare earth deposits and imports from China. Recent china rare earth export limitation looking for alternative sources of rare earth elements.

D. Alternative sources for rare earth elements

Yttrium was extracted from Korean coal ash by solvent extraction. This is the other alternative sources of rare earths. South Korea has found an undetermined amount of rare earth minerals in a deposit in the eastern Gangwon province, state-run Korea Resources Corp (KORES). The South Korean state-run mining firm discovered veins containing rare earths while re-developing an iron ore mine.

III. Yttrium Global Demand and its Applications

Yttrium oxide (Y_2O_3) is the critical enabler of energy efficient lamps, ubiquitous electronic devices, and other advanced materials used in defense, aerospace, energy infrastructure, and medical applications. Critical as it may be, the market is being hampered by a fog of uncertainty because of China's hegemony over global Y_2O_3 production [4].

Yttrium is quite used in ceramics, producing alloys, and optical glasses (See Figure 4). It is also used in special catalysts and in opto-electronic devices such as lasers, filters for microwaves and europium "phosphorus" for the red color in television sets. Some of its isotopes are radioactive, being used in cancer radiotherapy.

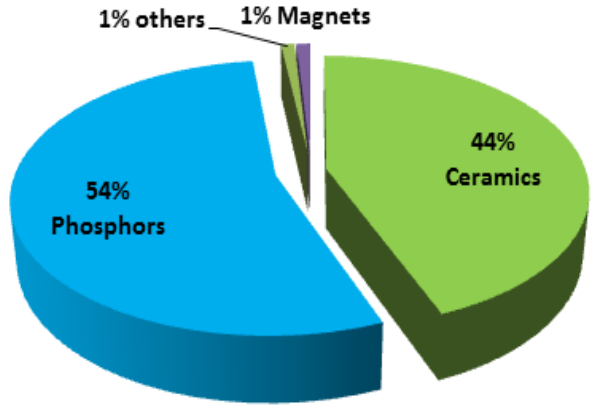

Fig. 4 Yttrium end use applications

IV. Yttrium Extraction from Coal Ash

Figure 5 showed the molecular structures of extractants. Figure 6 showed the flow sheet of yttrium extraction by using several kinds of extractants such as PC 88A, Cyanex 272 and Cyanex 302. Among these extractants PC 88A is more suitable for the yttrium extraction.

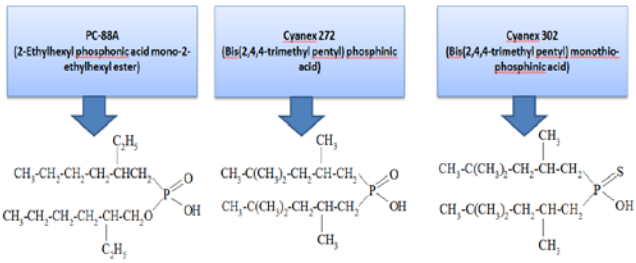

Fig. 5 Molecular structures of extractants

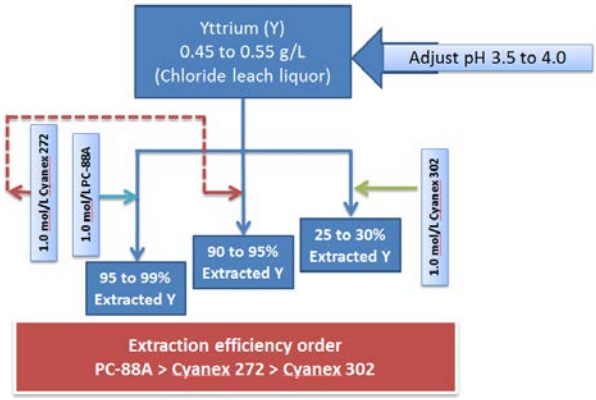

Fig. 6 Flow sheet of yttrium extraction(based on Literature Survey)

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Yttrium compounds have the following uses:

Yttrium oxide is used to produce yttrium iron garnets which are useful microwave filters. Yttrium oxide is used in ceramic and glass formulations as it has a high melting point and imparts thermal shock resistance and low expansion characteristics to glass

• Yttrium oxide is widely used for making compounds such as YVO4europium and YVO4europium phosphors which are responsible for the red colour in television tubes.

• Yttrium iron ($Y_3Fe_5O_{12}$), yttrium aluminium ($Y_3Al_5O_{12}$) and yttrium gadolinium garnets possess interesting magnetic properties. Yttrium iron garnets are extremely efficient transmitters and transducers of acoustic energy. Yttrium aluminium garnet has a hardness of 8.5 and is finding application as a gemstone (synthetic diamond)

V. Importance of Coal Ash Recycling

A. Environmental problem of Coal ash dumping

The process of coal combustion results in the generation of coal combustion residues (CCRs). Coal combustion residues (CCRs) include materials that are left over after the burning of coal. They are fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) materials (wet or dry).

Coal-burning pollutes the environment by releasing a wide range of toxins-sulfur, carbon monoxide, nitrogen oxide, carbon dioxide, Heavy metals- Hg, As, Pb and radioactive materials. Coal-fired plants generate tons of toxic residue and most of them is buried in landfills or stored in open ponds. In 2008, TVA Kingston Fossil Plant in Tennessee is holding pond failed and released 1.1 billion gallons of residue into nearby rivers.

B. Characteristics of REEs in World-wide produced Coal Ash

From the surveys of coal resource, some deposits may contain economically viable concentrations of rare elements. The combustion process of coal results in the enrichment of metal concentrations in the coal ash waste which is several times the concentration found in raw coals. The range of strategic metal concentrations in coal ashes, similar to those from mineral ores. Coal ashes are possible resources for metal recovery.

Here we reported the mean concentrations of coal ash from power plants in the U.S, Europe, Mexico and Spain, Russia, China [5]. It is clear from Table 1 that natural rare earths concentrations varies greatly among different kinds of coal and depends generally to ash content. Table 1 data showed the rare earths concentration in coal is lower than that of coal ash and it is the major evidence of the alternative source for rare earths.

Table. 1Mean concentration of coal ash from power plants (U.S, Europe, Mexico and Spain, Russia, China)

Element (mg/kg)	Raw Coal	Coal Ash	Coal Fly Ash
Ce	20.9	468	405-565
Dy	2.09	61.54	32.1-50.3
Eu	0.28	7.64	3.9-5.9
La	9.09	259.85	206-286
Nd	8.48	236.02	183-256
Pr	4.81	59.02	49.0-68.4
T b	0.54	10.29	4.9-73
Y	8.18	408.34	191-259
Ga	5.24	Limted	212-299
Ge	4.23	<10 -1841	1.00-356
Te	1.82	limited	0.14-2.7
Total REE	54.91	1723	1213.6-1667.6

As an representative example, Seredin and Dai (2012) researched that U.S., Chinese, and Russian coal source contain concentrations within the range of mineral ore deposits. So, Initial metal recovery from coal ash is more efficient than ore processing. Figure (7)[6]. shows the average concentration of Rare Earth Elements in World coal ash, representing high concentration of Y. Different regions have various sources of REE. For Coal Ash REEs Recycling, it is vital to study and classify the characteristics of REEs from coal ash comparing with the Origin of Coal regionally.

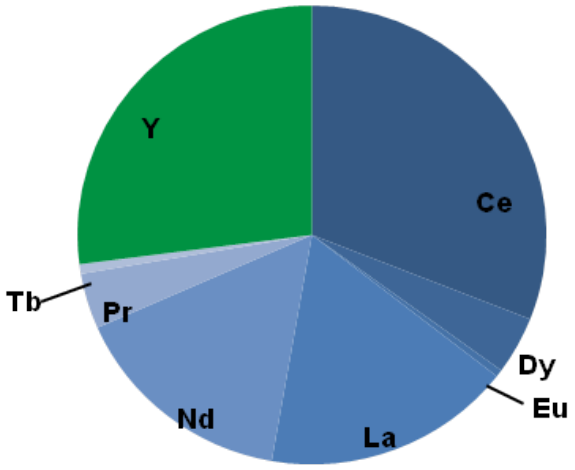

Fig.7 Unit: mg/kg; Mean of Concentration of coal ash from Power plants in the U.S, Europe, Mexico and Spain, Russia, China

C. Recovery REEs from Coal Ash

Raw unprocessed coal contains a variety of metals, and in some cases, enriched concentrations of some strategic elements. Surveys of coal resources indicate that some deposits may contain economically viable concentrations of rare elements. High commodity prices are encouraging development of processes to extract minerals, metals and rare earths from coal ash deposits. In such cases, recovered ash can supply high-demand materials (i.e.: alumina, magnetite, and germanium). Such new and emerging technologies allow resource recovery at an economically competitive cost.

The U.S produces 70 million new tons/year of fly ash. In the

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Laboratory investigation, Neumann Systems Group(NSG) successfully extracted near 60% of 11 Rare Earth Elements from and 99% of select REEs and ~99% CaO extraction. Since 2013, NSG has planned to produce 14,000 tons/year from Single Process Train Plant. 14 Rare Earth Elements were recovered and simultaneous removal of hazardous materials such as mercury and arsenic. The Extracted metals ranges between $400 to $750 per ton of fly ash. Basic extraction process, and supercritical carbon dioxide ($ScC0_2$) and a co-solvent extraction process. Scandium and Yittrium were selectively removed together by the supercritical carbon dioxide ($ScC0_2$) extraction process.

VI. Coal Power Plants and Coal Ash Production in South Korea

Fig. 8 shows the rate of coal fired power plant is increased by 6th Electric Supply Government Plan. 2.2% of annual electrical consumption will be increased as 6th Electric Supply Government Plan. So it will be hard to reduce the emission rate of Green-house gases with this value[7].

A. Coal Power Generation in South Korea

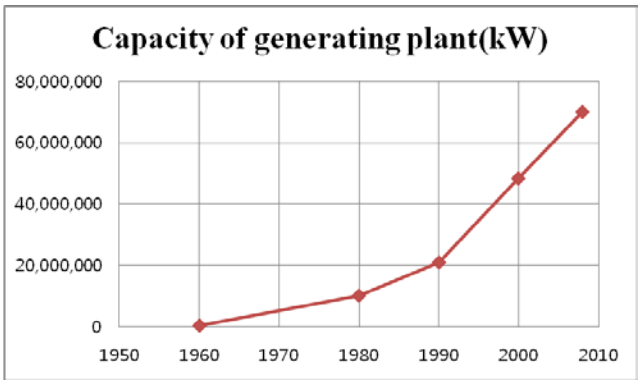

Fig. 8 Increased trends of construction of Coal-fired power plants in South Korea

B. Coal Ash Production in South Korea

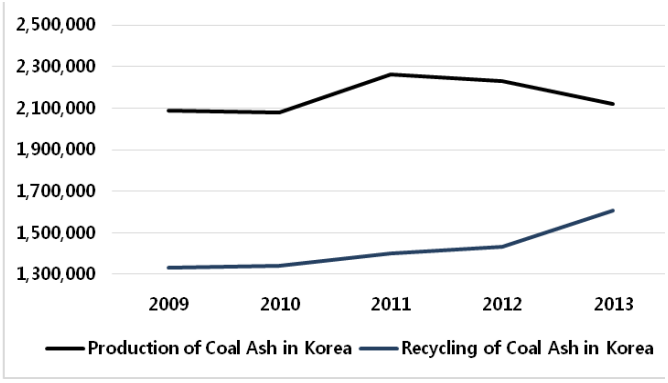

Fig.9 Production(Black) and Recycling(Blue) of Coal combustion product(Coal ash), South Korea.

Fig.9 shows production of coal ash from South-East Power Plant including Samcheonpo power plant, Yeongheung power plant, Yeongdong power plant and Yeosu power plant located in South-east part of South Korea (unit: ton)[8].

VII. The Status and Situation of Critical Elements in South Korea

REEs Market of Korean Industry is about 2,9658million $ scale. Korea imports REEs as half-finished or finished products.

Cerium is highly demanded critical element in Korea, especially for abrasives. Samsung Corning Co. and Hankuk Electric Glass Co. are occupying 74. 8% of Ce Industry in Korea. Korea imports 500 ton of Yttrium and Europium annually. Yttrium Oxide (Y_2O_3) and Europium (Eu_2O_3) are used for Red Color in the phosphor screen of the cathode ray tube in TV by Samsung SDI Co., LG Chem and Korea zinc. Wookyung Steel Co. contracts with CNC world, valued at $192million for supplying Yttrium Oxide in 2011. Samsung Electronics use Neodymium for Permanent Magnets. TMC Korea produces value-added nonferrous metals from scrap generate various sources including the secondary battery, super alloy, semiconductor, spent catalysts, samarium-cobalt magnet, titanium, zirconium, molybdenium, and other relevant materials. Also, Korea imports Ga from China, particularly Korea noble metals Co. imports, recycles and refines.

VIII. Experimental Results & Characteristics of REEs in Coal ash, South Korea

A. XRF & XRD experimental results of the samples.

Bottom ash (Tean) is provided Tean thermal power plant in South Korea. Fly Ash (Samcheonpo) is Samcheonpo power plant, located in South-east part of South Korea. Fly Ash(Japan) is provided from Japan for comparison(Table 2).

Table. 2. XRF Results of Coal Ash from South Korea & Japan

Wt.%	Bottom Ash (Tean)	Fly Ash (Samcheonpo)	Fly Ash (Japan)
SiO2	57.75	58.12	55.05
Al2O3	21.29	21.34	23.46
Fe2O3	8.74	6.58	7.06
CaO	4.31	4.52	4.8
MgO	1.34	1.91	1.94
K2O	1.07	1.15	0.94
Na2O	0.72	0.24	0.43
TiO2	0.13	1.09	1.31
MnO	0.09	0.08	0.09
P2O5	0.31	0.31	0.4
igloss	12.42	3.67	3.76

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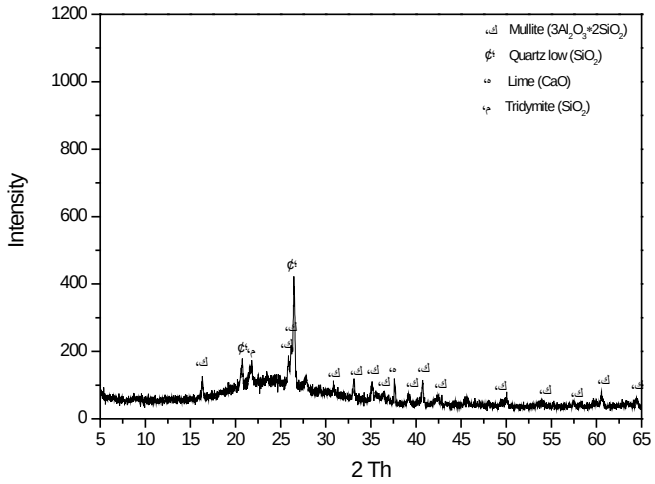

Fig. 10. XRD of Bottom ash (Tean)

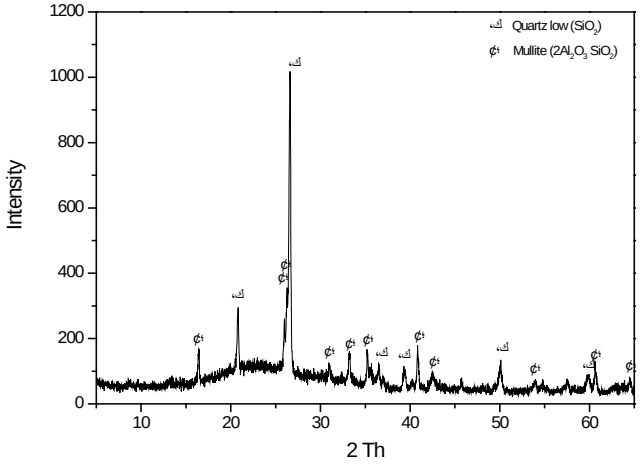

Fig. 11. XRD of Fly Ash (Samcheonpo)

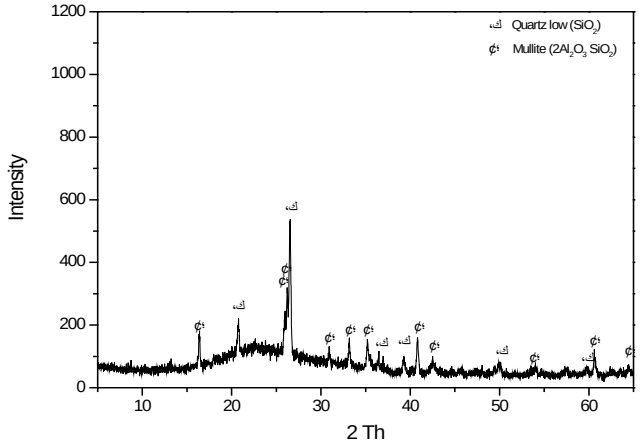

Fig. 12. XRD of Fly Ash(Japan)

B. REEs Concentration of Coal Ash samples

Table. 3 The concentration of REEs in bottom ash, fly ash and fly ash from Japan samples

Table. 3 The concentration of REEs in

	Bottom Ash (Tean)	**Fly Ash (Samcheonpo)**	**Fly Ash (Japan)**
(μg/g)			
Y	40	21.3	15.3
La	38.8	24.1	18.8
Ce	83.5	52.6	40.8
Pr	9.62	6.04	4.74
Nd	36	22.9	18.5
Sm	7.62	5.02	3.9
Eu	1.68	1.02	0.9
Gd	8.16	5.48	4.4
Tb	1.4	0.96	0.76
Dy	7.62	5.12	4.02
Ho	1.62	1.08	0.9
Er	4.56	3.24	2.56
Tm	0.7	0.48	0.4
Yb	4.42	2.9	2.44
Lu	0.72	0.46	0.38
Th	14.6	9.6	6.78
U	4.46	2.82	1.96

IX. CONCLUSION

China's control over the rare earth market, coupled with the growing world demand and the importance of Rare Earth Metals has caused many countries to develop concerns about the security of the Rare Earth Metals supply chain and DOE published Critical Materials Strategy. Significantly increasing of rare earth elements' price, rare earth requires a 'convergence technology' for the waste utilization from coal power plants and other key applications such as military defenses. Due to increase of coal power plant after Fukushima impact and abundance of world-wide coal reserves, recovery of rare earth critical elements from power plants waste ash (bottom ash, fly ash) is an ideal approach; it has been proved to be an effective way for CO_2 sequestration for CO2 reduction and stabilization of hazardous heavy metal by accelerated Carbonation.

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