International Journal of Coal Geology 94 (2012) 67–93

Contents lists available at SciVerse ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Review Article

Coal deposits as potential alternative sources for lanthanides and yttrium

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ARTICLE INFO

Article history:
Received 15 August 2011
Received in revised form 1 November 2011
Accepted 4 November 2011
Available online 11 November 2011

Keywords:
Coal deposits
Rare earth elements and yttrium (REY)
REY distribution
REY mode of occurrence

ABSTRACT

This paper presents data on widespread abnormal accumulations of lanthanides and yttrium (REY) in many coal deposits worldwide. High REY contents (>0.1%) have been found in coal seams and coal ashes, as well as in the host and basement rocks of some coal basins.

For a preliminary evaluation of coal ashes as an REY raw material, not only the abundance but also the individual REY compositions were taken into account in this paper. Three REY distribution patterns for high-REY coal ashes are fixed, with LREY- ($La_N/Lu_N > 1$), MREY- ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and HREY- ($La_N/Lu_N < 1$) enrichment. Four genetic types of REY enrichment in coal basin can be identified: 1) terrigenous type, with REY input by surface waters; 2) tuffaceous type, connected with falling and leaching of acid and alkaline volcanic ash; 3) infiltrational or meteoric ground water driven type, and 4) hydrothermal type, connected with ascending flows of thermal mineral water and deep fluids. It is shown that the main modes of REY occurrence in high-REY coals are in fine-grained authigenic minerals (REY-bearing aluminum phosphates and sulfates of the alunite supergroup, water-bearing phosphates and carbonates) and organic compounds. Stratabound and cross-cutting REY mineralization may occur in the host and basement rocks of some coal basins. There are tuffaceous and hydrothermal types of REY mineralization outside coal seams that are significantly different in geological settings, ore body shapes, and ore compositions, as well as in REY contents and distribution patterns. The data presented indicate that coal deposits should be regarded as promising objects for recovery of REY as economic by-products of coal mining and combustion. As REY are crucial metals for alternative power and energy-efficient technologies, identification of these resources during coal exploitation and utilization may not only increase beneficiation of coal deposits themselves but also will promote humanity's further movement on the "green road".

Contents

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doi:10.1016/j.coal.2011.11.001

1. Introduction

The first suggestions about possible recovery of lanthanides and yttrium (REY) as by-products from coal deposits can be traced back to 20 years ago, after the discovery of coal beds with high REY content (0.2–0.3% in ash) in one of the Russian Far East (RFE) coal basins (Seredin, 1991). During the next five years, several coal seams with similar and even higher REY contents (up to 1.0% in ash) were discovered in six coal-bearing basins of this region (Seredin, 1996). Since then, REY-rich coals have been found in other coal basins in a number of countries (Arbuzov et al., 2000; Dai et al., 2007, 2008, 2011b; Hower et al., 1999; Mardon and Hower, 2004; Nifantov, 2003; Seredin, 2004; Seredin et al., 2006b). Moreover, high REY contents were also detected outside coal seams in some basins (Dai et al., 2010a, 2010b, 2011a; Koldaev and Bezdeliga, 2011; Seredin, 1998, 2004, 2006; Seredin and Tomson, 2000; Seredin et al., 2006a, 2006b). In a few cases, the REY content in the underlying basement rocks may be as high as 4–11% (Seredin et al., 2009).

However, these unusual REY anomalies in coal basins have not attracted special attention, because it seemed that there were sufficient resources of these metals in conventional deposits (e.g., carbonatites, alkaline granites, and weathering crusts). This situation has changed considerably since 2009, however, as the world economy met with a crisis concerning REY supply (Lifton, 2009). The causes of this crisis and possible ways to overcome REY shortages were widely discussed in the mass media, websites (http://www.techmetalsresearch.com; http://www.raremetalblog.com, etc.), and at numerous international conferences. Common opinion suggests that there is no other way to address this problem than prospecting for and exploiting new ore deposits, which is now being carried-out in many countries; however, the focus still remains on exploration for conventional REY deposits.

In the present work, literature data and the authors' work on REY anomalies in coal basins are generalized, with the aim of elucidating whether coal deposits may represent new potential sources for REY metals. REY recovery as a by-product from coal deposits actively mined in many countries could alleviate the current raw material crisis and, from the environmental point of view, make "dirty" coals into an REY source for "clean" energy.

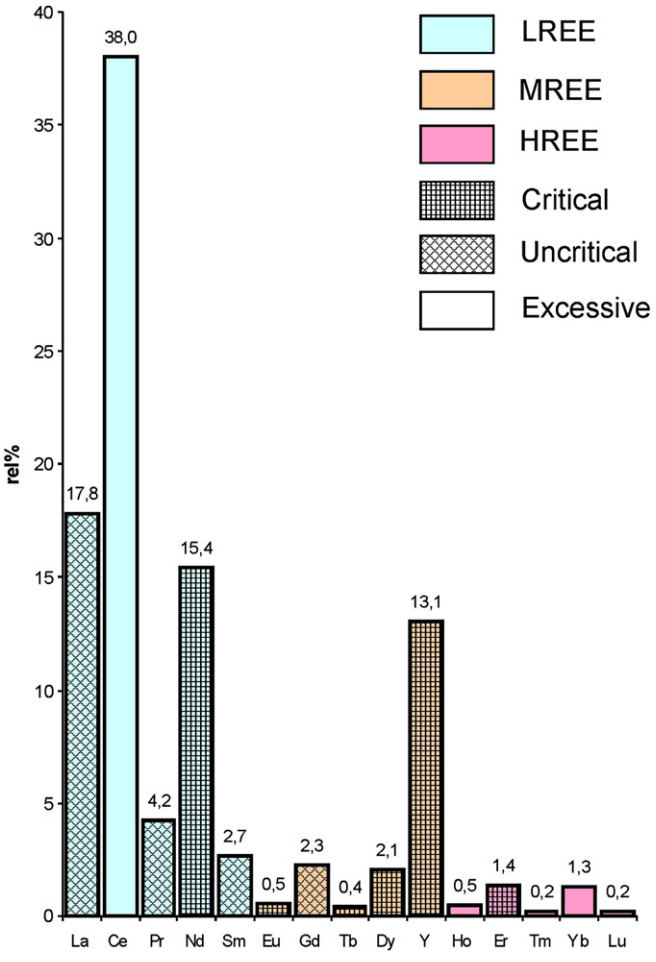

Fig. 1. Percentage share of various REY in total REY composition of the Upper Continental Crust (after Taylor and McLennan, 1985) and their classifications.

2. REY: classification, significance, sources, and problems

2.1. Classification

There are several classifications of these elements from geochemical and economic points of view (e.g. Hatch, 2009; Seredin, 2010 and references therein). Two classifications are used in the present study.

The first is a geochemical classification, which divides REY into light (LREY — La, Ce, Pr, Nd, and Sm), medium (MREY — Eu, Gd, Tb, Dy, and Y), and heavy (HREY — Ho, Er, Tm, Yb, and Lu) groups. The threefold geochemical classification, as described below, is more convenient than the other classifications for the description of REY distribution both in coals and in conventional REY ores. Yttrium is closely associated with lanthanides in nature, because both its ionic radius is very similar and its ionic charge is equal to that of Ho. For this reason, yttrium is generally placed between Dy and Ho in normalized REY plots (Bau, 1996).

For evaluation of coals as REY raw materials, a threefold market or industrial classification was used in this study. The classification is based on the Dudley Kingsnorth (IMCOA) forecasts of the relationship between demand and supply of individual REY in recent years (Kingsnorth, 2009). According to this classification, REY are divided into critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd) and excessive (Ce, Ho, Tm, Yb, and Lu) groups (Seredin, 2010). The relation of the two classifications is illustrated in Fig. 1.

2.2. REY roles in the modern world

Due to their unique magnetic, luminescent, and chemical properties, REY play a key role in the manufacture of materials and products (from household to defense purposes) that provide a modern