

Review article

Chlorine in coal: A review

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Abstract

This review embraces approximately 100 publications on chlorine (Cl) in coal. Topics reviewed in this paper include: (a) historical introduction; (b) some peculiarities of Cl environmental geochemistry; (c) estimation of the Cl coal Clarke value; (d) occurrence of high-Cl coals; (e) mode of Cl occurrence in coal; (f) factors influencing the distribution of Cl in coal; and (g) origins of Cl in coal.

1. The world average Cl contents in coals (coal Clarke of Cl) for hard and brown coals are, respectively, 340 ± 40 and 120 ± 20 ppm. The average Cl content on an ash basis is 1435 ppm which is much more than the Clarke value for sedimentary rocks (150 ppm); hence, chlorine is, on average, a highly coalphile element. Just this alone shows that the authigenic sorption fraction, Cl_{sorb} , must be dominant in coals.

Aside from “normal” coals with average Cl contents, there are “saline” coals, strongly enriched in Cl, up to 1 wt.% and more. Although there are different genetic concepts, it seems that such coals were mainly formed in epigenesis — when coal beds were influenced by basinal chloride brines (often by hot ore-forming brines, containing also some ore elements such as As, Pb, Zn, etc.).

The modes of Cl occurrence in coal are surprisingly varied. Among them are found inorganic salt-like Na and other chlorides, as well as the Cl-bearing silicates, carbonates, sulfides, as well as dissolved chlorides in pore moisture. Organic-associated Cl seems to predominate in coal. It may consist of two different types. One (minor) site (“true” Cl_{org}) may be as covalent-bonded Cl in coal organic macromolecules. The major organic Cl is represented by “semi-organic” Cl, as anion Cl^- , sorbed on the coal organic surface in pores and being surrounded by pore moisture. These are HCl-complexes bonded with bases, such as quaternary nitrogen.

If Cl in coal is mainly of syngenetic origin, a “true” Cl_{org} form may be of value, and Cl is concentrated in low-ash gelified coal macerals. If coals were submerged by epigenetic impact from basinal brines, Cl_{min} (NaCl and other salts) and “semi-organic” Cl_{sorb} forms have to be dominant. In such instances, Cl may be enriched in fusain and in high-ash coals.

There is a complicated relationship between Cl-contents in coal and coal rank. On the one hand, the coals subjected to epigenetic brine influence are, as a rule, bituminous coals that have been submerged to considerable depths where basinal brines exist. On the other hand, if coals have a rank higher than low volatile bituminous A (C^{daf} more than 86%), the Cl content decreases due to decreasing sorption capacity of the high carbonized coal organic matter.

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1. Introduction

Chlorine in coal first provoked an interest at the start of 20th century in England. In 1930's–1940's, with this country having many Cl-bearing coals, intense studies were performed concerning Cl distribution and mode of Cl occurrences in coal. A large part of these studies were outlined in the review by [Kear and Menzies \(1956\)](#) — the most complete by the end of the 1950's. Also, our previous outline ([Yudovich et al., 1985](#)) was mostly based on that review. Further studies added little new data about Cl contents in

coals, but highlighted some problems concerning Cl mode of occurrence in coal. The revolutionary studies of [Huggins and Huffman \(1991, 1995\)](#) must be especially noted.

2. Chlorine in environment

Chlorine has a high “marine-affinity”; its average content in sea water contents (1919 mg/L) is three orders-of-magnitude higher than that in fresh waters (5.5 mg/L) ([Ivanov, 1994](#), p. 292). However, Cl differs sharply from F because its highest mobility is in the

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