別記様式第３号－１

学 位 論 文 の 要 旨

氏　　名	古園　拓也
学位論文題目	石炭燃焼プラントにおける微量元素の分配挙動と 石炭灰からの溶出挙動解明

本論文は、石炭燃焼プラントにおける微量元素の分配挙動と石炭灰からの溶出挙動解明と題し、石炭燃焼におけるセレンやホウ素に着目し、プラント内での分配や石炭灰からの溶出など石炭燃焼に伴う微量元素の挙動を系統的にまとめたものである。

第1章は緒論であり、我が国の一次エネルギー供給における石炭の位置づけ、石炭利用における一般的な課題や微量元素に関する課題などを明確にした上で、セレンやホウ素をはじめとする微量元素の法規制、燃焼に伴う微量元素の揮発挙動、石炭灰への微量元素吸着挙動、石炭灰からの微量元素溶出挙動に関して既往の研究例を解説するとともに、本研究の意義を明らかにし、本研究の目的および構成を述べた。

第2章では、石炭燃焼プラント内のセレン挙動のうち、石炭燃焼におけるセレンの灰への分配について、既往の研究で開発した排ガス中のセレン分析手法を用いて、燃焼試験炉でその挙動を検討した。実験には、セレン含有量や燃料比、灰組成などの性状が異なる5種類の石炭を用い、セレンの灰への分配挙動について、石炭性状や燃焼条件、温度の影響を評価した。その結果、温度の低下に伴い粒子状セレンの割合が増えることを確認するとともに、炭種によって温度低下に伴う粒子状セレンの割合変化に大きな差があることを確認した。

そこで、300℃以上の領域と300℃以下の領域で灰への移行に影響するパラメータを検討した。300℃以上の領域では、石炭灰に含まれる鉄やカルシウムなどの量とセレンの分配に相関があること、300℃以下の領域では、灰の粒径や燃焼条件（灰中未燃分）とセレンの分配に相関があることを明らかにした。このことから、石炭灰への化学吸着と物理吸着がセレンの分配に影響を与えることを明らかにした。また、300℃以下の領域での物理吸着がセレンの分配挙動に支配的であることを明らかにした。

第3章では、石炭灰や微粒子中に含まれるセレンやホウ素について、2章などで明らかにした灰への分配挙動をもとに、灰中に含まれる化学形態を考慮した上で、これらの元素の分析に際する最適な前処理条件を検討した。具体的には、実機発電所や燃焼試験炉で採取した石炭灰を用いて、石炭灰の成分の違いに着目した検討を行った。石炭灰中の微量元素を分析するには､試料中のシリカやアルミナなどを完全分解するためにフッ酸を使用してきたが、石炭灰や微粒子中に含まれるセレンは、表面に吸着しているものがほとんどであり、フッ酸を用いた完全分解を行う必要がないこと、一方でホウ素は、石炭灰中の酸性成分（SiO_2, Al_2O_3, TiO_2）およびアルカリ成分（Fe_2O_3, CaO, MgO, Na_2O, K_2O）の量によって前処理時に必要なフッ酸の量が異なることを明らかにした。併せて、微粒子は石炭灰と比べて酸性成分の量が少ないことから、微粒子中のホウ素分析にはフッ酸は必要ないことを明らかにした。最適化した前処理法を利用し、セレンやホウ素をはじめとするさまざまな微量元素の微粒子への濃縮挙動について検討した。最適化した前処理条件で前処理を行い、微粒子への微量元素濃縮を検討した結果、発生割合は炭種によって異なること、また、セレンやホウ素は、微粒子へ濃縮することを確認した。

第4章では、石炭灰中の微量元素に着目し、セレンをはじめとする微量元素の溶出挙動について検討するとともに、近年、日本で使用されている低セレン炭の石炭灰に着目し、セレンの溶出挙動を詳しく解析した。併せて、石炭灰を湿潤状態に保つこと（エージング）によるセレンをはじめとする微量元素の溶出抑制技術について検討した。実験には、発電所や燃焼試験炉で採取された23種類の石炭灰を用いた。検討の結果、日本で近年発生する低セレン石炭灰を溶出試験した際のセレン溶出量は、石炭灰中のセレン含有量に依存すること、低セレン石炭灰からのセレン溶出量は、土壌環境基準を超える場合があるため対策技術が必要であることを明らかにした。また、エージングにより、水不溶性の遊芸元素オキソ酸含有エトリンガイトが生成し、石炭灰からの微量元素溶出抑制に繋がることが既に明らかになっている。しかし、セレン溶出抑制効果の高い石炭灰と低い石炭灰が存在し、抑制効果に違いが生じる理由は明らかになっていなかった。そこで本研究では、石炭灰中のCa, Al, Sの含有量より推定されるエトリンガイトの生成量に着目して検討した。その結果、エトリンガイト推定生成量とセレン溶出抑制効果に正の相関が見出された。エトリンガイト推定生成量は、エージングにより生成したエトリンガイト量をXRD、TGで測定して確認された。以上より、石炭灰中のCa, Al, S, Se含有量から、エージングによるセレン溶出削減効果を予測できることが示唆された。

第5章では、本研究により得られた成果を総括としてまとめた。

別記様式第４号

Summary of Doctoral Dissertation

Title of Doctoral Dissertation:

Clarification of partitioning behavior of trace elements in coal combustion plant and their elution behavior from coal ash

Name: Furuzono Takuya

This dissertation's subject is "Elucidation of the partitioning behavior of trace elements in a coal combustion plant and their elution behavior from coal ash," in which selenium and boron in coal combustion are focused on and the behaviors of trace elements associated with coal combustion, including their partitioning in a plant and their elution from coal ash are systematically summarized.

Chapter 1 is an introduction section, where after being described the positioning of coal in the primary energy supply in our country, general issues in coal use, the issues related to trace elements, and so forth, in regard to the legal restraints on trace elements including selenium and boron, the volatile behaviors of the trace elements associated with coal combustion, the adsorption behaviors of trace elements on coal ash, and the elution behaviors of trace elements from coal ash, previous study examples are explained to define the significance of this study, and also the objectives and composition of this study are described.

In Chapter 2, out of selenium behaviors in a coal combustion plant, as for the partitioning of selenium to ash in coal combustion, by using the method to analyze selenium in flue gas, which has been developed through previous studies, the behaviors of selenium were examined with the use of a combustion test furnace. In the test, five kinds of coals with different properties in selenium content, fuel ratio, ash composition, and others were employed, and as for the partitioning behaviors of selenium to ash, the coals' properties, combustion conditions, and the influences of temperatures were evaluated. As a result, it was confirmed that the ratio of selenium in solid phase is increased associated with a decrease in temperature and also that the transition of the ratio of selenium in solid phase associated with a decrease in temperature significantly varies depending on coal type. Accordingly, the parameters influencing the transition to of selenium to ash were examined in the area where temperature is 300℃or above and in the area where temperature is 300℃ or below, respectively. The examination proved that in the area where temperature is 300℃ or above, there is a correlation between the amounts of iron, calcium, and others contained in coal ash and the partitioning of selenium, and also that in the area where temperature is 300℃ or below, likewise, combustion conditions (unburned carbon in ash) have a correlation to the partitioning of selenium. That is, the test proved that the partitioning of selenium is influenced by chemical or physical adsorption on coal ash. Additionally, the test revealed that the partitioning behaviors of selenium is dominantly influenced by the physical adsorption in the area where temperature is 300℃ or below.

In Chapter 3, as for selenium and boron contained in coal ash and fine particles, after considering the

chemical forms of the elements contained in ash based on the partitioning behaviors of them to ash which have ever been found, the optimum pretreatment conditions for analyzing the elements, selenium and boron in coal ash were examined. Concretely, by using coal ash collected in a commercial power plant or a combustion test furnace, the study focused on the differences in the components of coal ash was implemented. In the previous studies, in order to analyze the trace elements in coal ash, hydrofluoric acid was used to be employed due to the complete decomposition of silica, alumina, and others in samples. However, in the current study, it was found that most of selenium contained in coal ash and fine particles tend to adsorb onto the surfaces of them and therefore there is no need to apply the complete decomposition with the use of hydrofluoric acid. On the other hand, it was also found that the amount of hydrofluoric acid needed at the time of the pretreatment of boron varies depending on the amounts of acid components (SiO_2, Al_2O_3, TiO_2) and alkaline components (Fe_2O_3, CaO, MgO, Na_2O, K_2O) in coal ash. Furthermore, the study proved that hydrofluoric acid is unnecessary for the analysis of boron in fine particles because the particles are lower in acid component than coal ash. Moreover, by using the optimized pretreatment method, the concentrated behaviors of various trace elements including selenium and boron to fine particles were examined. As a result that the pretreatment of the trace elements was conducted under the optimized pretreatment conditions to examine the concentration of the elements to fine particles, it was confirmed that the generation rate of fine particles (generated due to coal combustion) varies depending on coal type and that selenium and boron are concentrated into fine particles.

In Chapter 4, the trace elements in coal ash were focused on to examine the elution behaviors of trace elements including selenium, and additionally, coal ash from low selenium coal which has been recently used in Japan was focused on to analyze the elution behaviors of selenium circumstantially. Furthermore, technologies to control the elution of trace elements including selenium through aging treatments were also examined. In a test, 23 kinds of coal ash, which were collected from a power plant or a combustion test furnace, were employed. As a result of examination, it was revealed that the elution amount of selenium obtained when the dissolution test of low selenium coal ash is conducted, which has recently occurred in Japan, depends on the selenium content in coal ash and that because in some cases, the elution amount of selenium obtained from low selenium coal ash exceeds soil environmental standards , the countermeasure technology for the control of selenium elution is necessary. Additionally, it has already been clarified that aging treatments for coal ash produce a water-insoluble trace element, oxyacid-containing Ettringite, which leads to the control of the elution of trace elements from coal ash. However, there are coal ash with high inhibiting effect on selenium elution and one with low effect on the elution, and the reason why the inhibiting effect differs depending on each coal ash has not been cleared up. Therefore, in this study, we examined the effect focusing on the production of Ettringite that is estimated from the contents of Ca, Al and S in coal ash. As a result, a positive correlation was found between the presumed production of Ettringite and the inhibiting effect on selenium elution. The presumed production of Ettringite was confirmed by measuring the amount of Ettringite produced through aging treatments with XRD (X-ray diffraction) and TG (tomography). From the above, it was suggested that the reduction effect of selenium elution through aging treatments can be predicted based on Ca, Al, S, and Se contents in coal ash.

In Chapter 5, the results obtained through this study are generally summarized.