

Electrochemical Reduction of Vitrified Nuclear Waste Simulants in Molten Salt

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Chapter 1

General introduction

1.1 Energy trend and situation of nuclear power

The amount of energy consumption is increasing year by year with the growth of population in the world. [Figure 1-1](#) shows the trend of world electricity generation from 1971 to 2015 by power source [\[1\]](#). Fossil fuels of coal, oil, and natural gas have been the dominant energy resources for a long time. However, these conventional resources have the limitation and

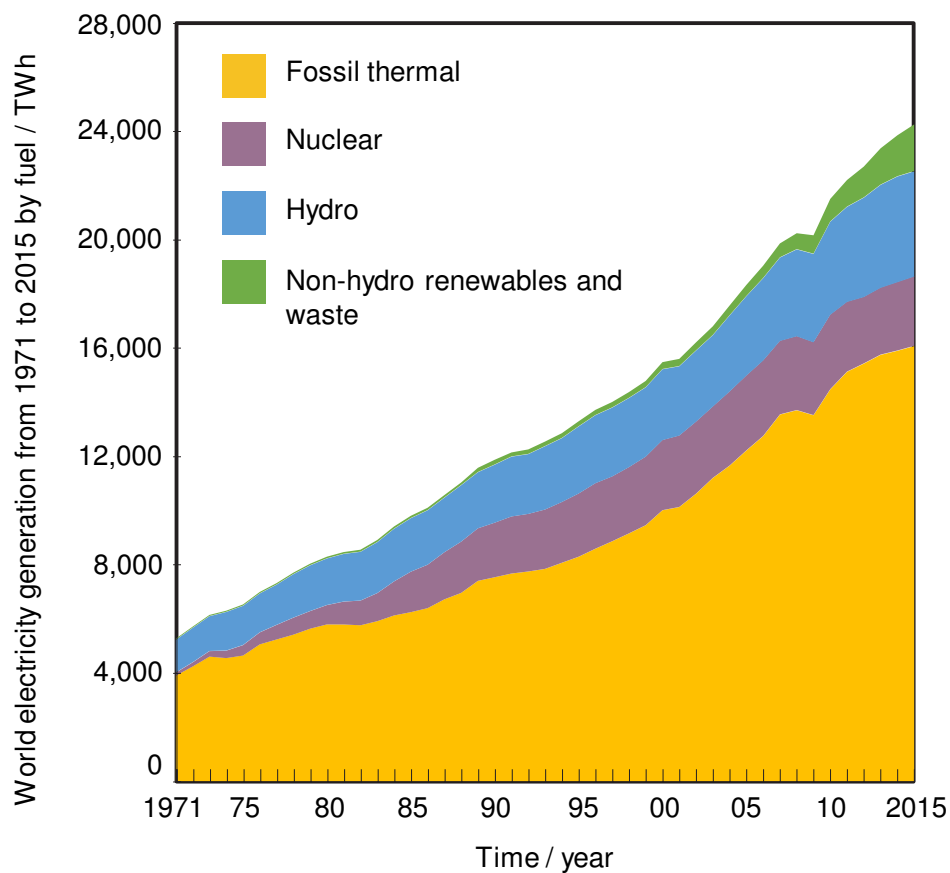


Figure 1-1 World electricity generation1 from 1971 to 2015 by fuel (TWh) [\[1\]](#).

emit a large amount of carbon dioxide (CO₂) which causes the global warming. Therefore, the establishment of alternative power supply system free from conventional fossil fuels is required.

The nuclear power generation can produce a huge amount of energy from a small amount of fuel, and can suppress the amount of CO₂ emission compared to other conventional power generation methods. In particular, since Japan is well known as a resource-poor country, it is critically important to improve the energy self-sufficiency ratio by lowering the dependence on fossil fuels.

Table 1-1 shows the life cycle CO₂ equivalent for some selected electricity supply technologies [2,3]. The large CO₂ emission per 1 kWh power generation for the conventional fossil fuels increases the concern of global warming. Although the values of life cycle CO₂ equivalent are relatively small for the renewable energy resources, these power generations cannot meet the

Table 1-1 Life cycle CO₂ equivalent including albedo effect from selected electricity supply technologies. Arranged by decreasing median (gCO₂eq/kWh) values [2,3].

Technology	Life cycle CO ₂ equivalent		
	Min.	Median	Max.
Currently commercially available technologies			
Coal– pulverized coal	740	820	910
Biomass– cofiring with coal	620	740	890
Gas–combined cycle	410	490	650
Biomass – dedicated	130	230	420
Solar PV– utility scale	18	48	180
Solar PV– rooftop	26	41	60
Geothermal	6	38	79
Concentrated solar power	9	27	63
Hydropower	1	24	2200
Wind Offshore	8	12	35
Nuclear	4	12	110
Wind Onshore	7	11	56
Pre-commercial technologies			
CCS– Coal – pulverized coal	190	220	250
CCS – Coal – integrated gasification combined cycle	170	200	230
CCS – Gas – combined cycle	94	170	340
CCS – Coal –oxyfuel	100	160	200
Ocean (tidal and wave)	6	17	28

high energy demands at this moment because of the problems of unstable power supply, low efficiency, high cost, and limited places. Therefore, nuclear power has potential as base-load power to accommodate the energy demand without emitting a large amount of CO₂.

At the end of 2015, the reserve-to-production ratios (RPRs) of energy resources are around or less than 100 years. For example, RPRs of oil, gas, and coal are 51 years, 53 years, and 114 years, respectively [4]. However, the acceleration of energy demand in developing countries will reduce these RPRs. Although the RPR of uranium is estimated to be 102 years in the case of light-water reactors (LWR) [5], the length will be extended to 1,000–10,000 years by utilization of fast-breeder reactors (FBR) [6]. Further development of nuclear power generation, such as a fundamental shift from the current process called “once-through fuel cycle” to FBR or other innovative system, is necessary to secure the energy in the future.

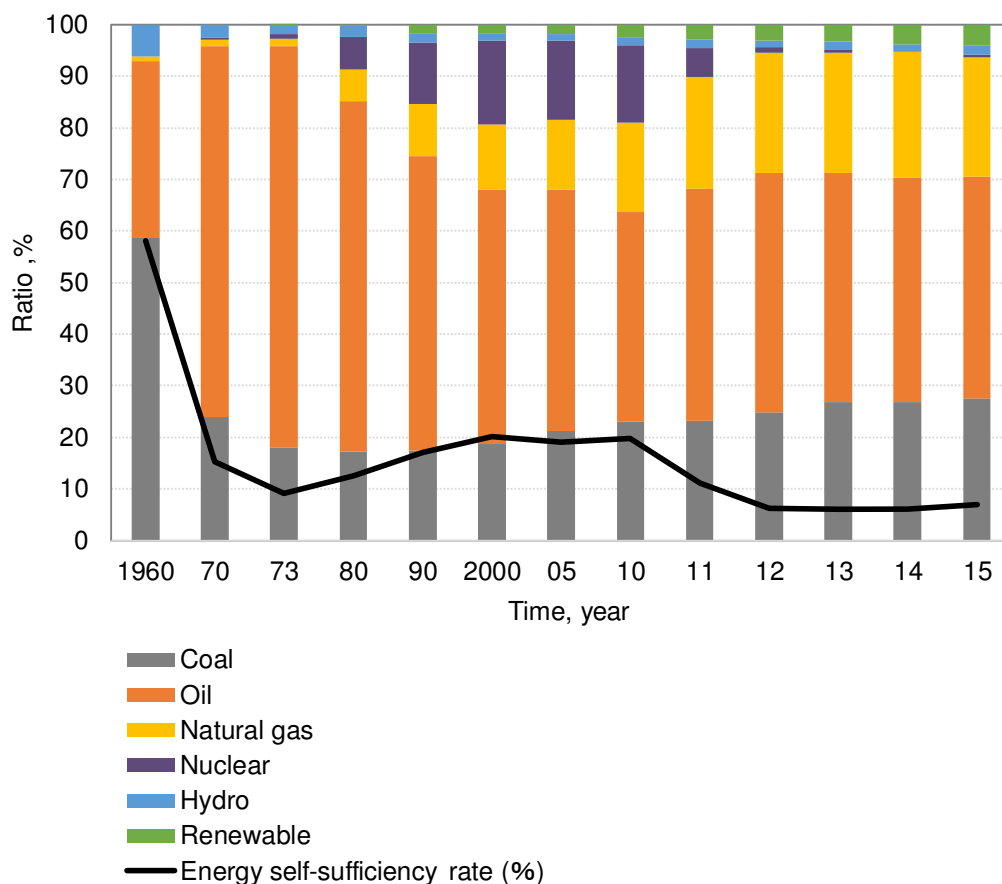


Figure 1-2 Trend of energy generation ratio in Japan from 1960 to 2015 [7].

The trend of energy generation ratio in Japan from 1960 to 2015 is shown in [Figure 1-2 \[7\]](#). The ratio of nuclear power generation has been increasing since the oil shock in 1973. After Fukushima Daiichi Nuclear power disaster in 2011, the operation of all nuclear power plants had been stopped, and the current ratio of nuclear power is still small. On the other hand, the global amount of nuclear power has been increasing, even after 2011 as shown in [Figure 1-1](#). 10.6 % of the global electric power are supplied by the nuclear power generation in 2015 [\[1\]](#). [Table 1-2](#) shows the nuclear energy consumption for each country in 2016. US is the largest nuclear energy using

Table 1-2 Nuclear energy consumption by country in 2016 [\[4\]](#).

Country	Nuclear energy consumption / Mtoe
US	191.8
France	91.2
China	48.2
Russian Federation	44.5
South Korea	36.7
Canada	23.2
Germany	19.1
Ukraine	18.3
United Kingdom	16.2
Sweden	14.2
Spain	13.3
Belgium	9.8
India	8.6
Taiwan	7.2
Czech Republic	5.5
Finland	5.3
Switzerland	4.8
Japan	4.0
Hungary	3.6
South Africa	3.6
Brazil	3.6
Bulgaria	3.6
Slovakia	3.3
Romania	2.6
Mexico	2.4
Argentina	1.9
Other Europe & Eurasia	1.8
Iran	1.4
Pakistan	1.3
Netherlands	0.9

country, dominating the 32 % of the total nuclear power generation in the world. The second largest country is France: 72 % of domestic power is supplied by nuclear energy in 2016.

The status of nuclear energy development in each country in 2017 [8,9] is shown in Figure 1-3. Although Germany has decided to phase out the nuclear power by 2022, new reactors are under construction in several developing countries such as China and India. Thus, the global nuclear energy is expected to increase in the future.

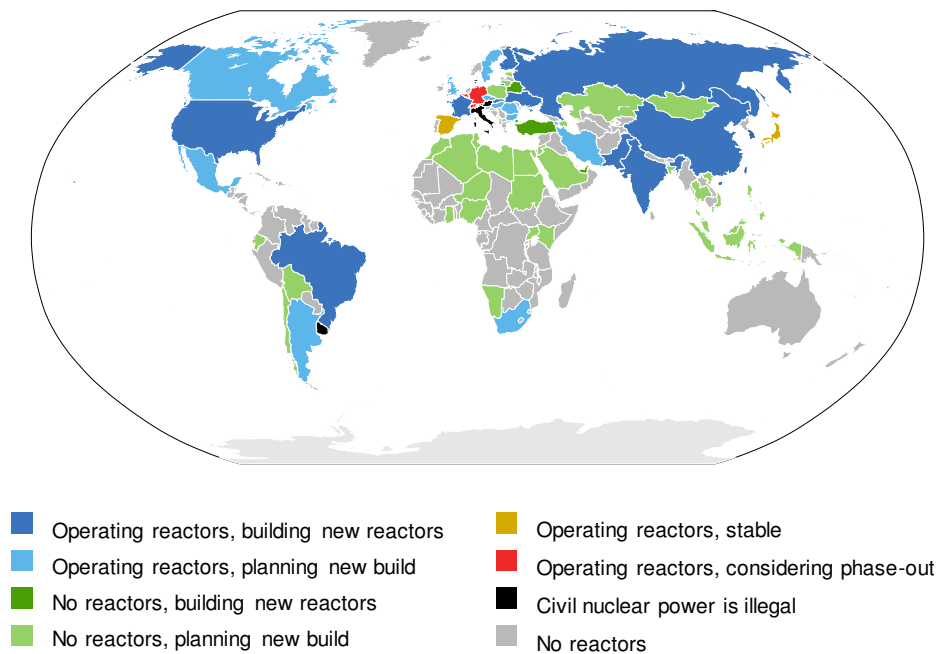
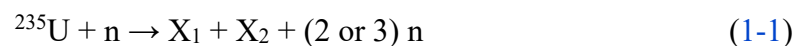


Figure 1-3 Global status of nuclear energy development in 2017 [8,9].

1.2 Nuclear power generation

In nuclear power generation, a fission reaction by an interaction between a neutron and a fissile nucleus such as ^{235}U is utilized for energy production.



In this reaction, two nuclei (X_1 and X_2) are generated as fission products along with a few neutrons.

Moreover, the mass defect generates enormous amount of energy in the nuclear reaction. For example, the fission reaction of one ^{235}U atom generates *ca.* 200 MeV, which means that 1 MWd (8.64×10^{10} J) is produced by mass defect of 1 g of ^{235}U . The practically obtainable energy in a neutron capture of ^{235}U to form ^{236}U is 6.74×10^{10} J, which is 2 million times as large as the energy produced by burning of 1 g coal [10].

Natural uranium is mainly composed of ^{238}U and ^{235}U . Uranium ore contains *ca.* 99.3% of ^{238}U and *ca.* 0.7% of ^{235}U . Table 1-3 lists the production of uranium ore by country in 2016. A large proportion of uranium ore are produced by amount ten countries. Major uranium ores are pitchblende and uraninite (uranium oxide). There are various smelting processes of uranium ore to obtain uranium. One method is acid leaching in which uranium contained in the ore is leached out to acids. After several processes, uranium concentrate powder called as yellowcake is obtained. Yellowcake is converted to UF_6 . In the enrichment process, ^{235}U is enriched by a centrifugal

Table 1-3 **Production of uranium ore by country / tons in 2016 [11].**

	(2016)
Country	Production of ore (tonnes U)
Kazakhstan	24575
Canada	14039
Australia	6315
Niger	3479
Namibia	3654
Russia	3004
Uzbekistan (est)	2404
China (est)	1616
US	1125
Ukraine (est)	1005
South Africa	490
India (est)	385
Czech Republic	138
Romania (est)	50
Pakistan (est)	45
Brazil (est)	44
Total world	62,366
Equivalent tonnes U_3O_8	73,548
Ratio to world demand	98%

separation of UF_6 gas. Then, UF_6 gas is reconverted to UO_2 powder to fabricate fuel pellets containing 95% UO_2 . UO_2 pellets are filled in zircalloy cladding tubes to be fuel pins. Many aggregated pins are set in nuclear reactors.

Uranium nuclear fuel contains ^{238}U and ^{235}U as radioactive materials. The ratio of ^{235}U has to be increased up to 3–4% from 0.7% in natural uranium, which is called an enrichment. More than 80 % of the nuclear power was generated by LWRs in the world in 2012. In LWR, 2–3% ^{235}U low-enriched uranium fuel is used. In FBR, 15–30 % high-enriched plutonium fuel is used to keep the chain reaction.

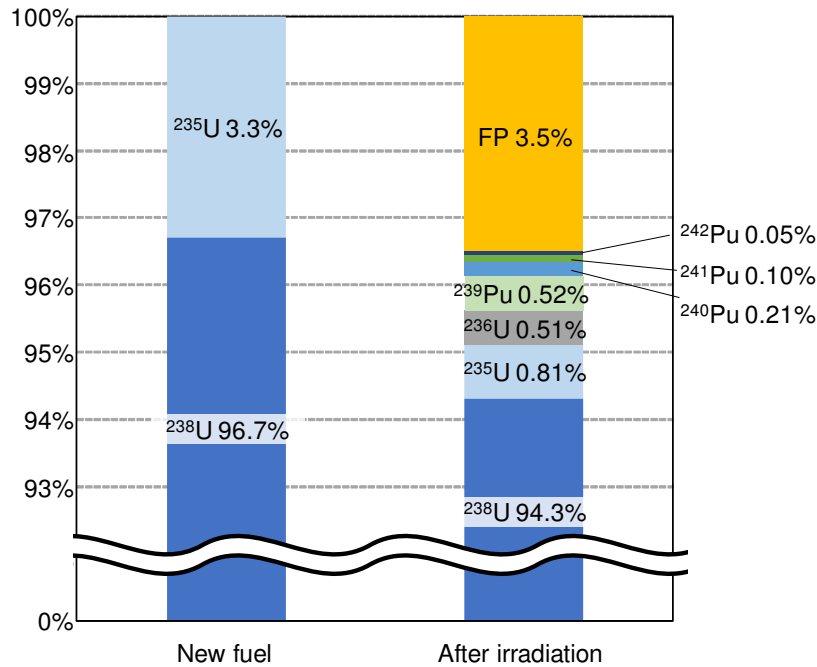


Figure 1-4 Composition of nuclear fuel before and after power generation [12].

Figure 1-4 shows the composition of radioactive materials in uranium fuel before and after power generation [12]. After power generation, ^{238}U , ^{235}U , and 3–5% of fission products (FPs) exist in the fuel. More than 300 kinds of FPs are produced as primary products by the fission reaction between uranium and thermal neutron [12]. Figure 1-5 shows the relationship between yield and mass number of FPs produced by the fissions of ^{233}U , ^{235}U , and ^{239}Pu by thermal neutron [13]. The mass distribution of FPs has two yield peaks at 95 and 140. Thus, some nuclides with

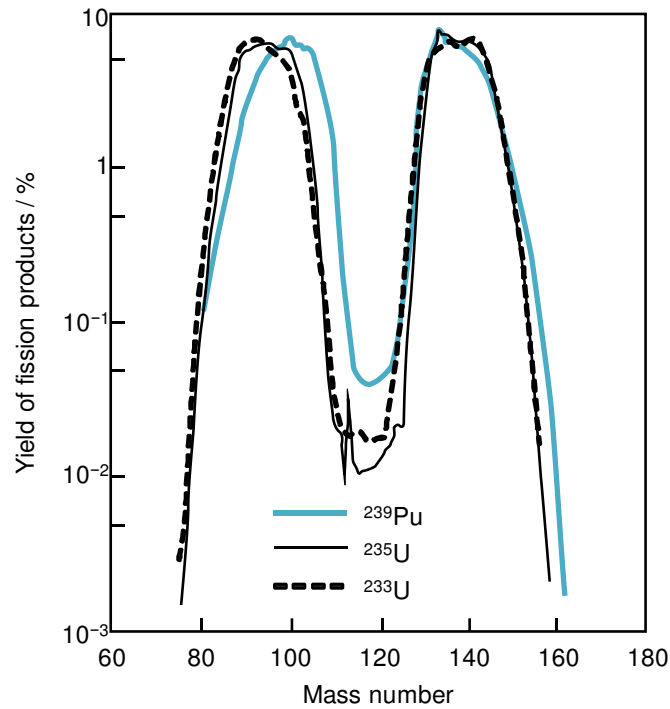


Figure 1-5 The mass distribution of yield of FP produced from interaction of ^{233}U , ^{235}U , or ^{239}Pu and thermal neutron [13].

high yields bring serious problems in the case of accidents. For example, ^{134}Cs (half-life period: $t_{1/2} = 2.1$ yr.), ^{137}Cs ($t_{1/2} = 30.1$ yr.), and ^{131}I ($t_{1/2} = 8.0$ days) widely polluted the environment in the Fukushima Daiichi nuclear disaster. ^{90}Sr ($t_{1/2} = 28.8$ yr.) was contained in the radioactive water from nuclear power plants in Fukushima.

The disposal methods of spent nuclear fuel are classified as “direct disposal” and “reprocessing and recycle”. In the direct disposal method, the spent nuclear fuels with uranium, plutonium, and FPs are disposed directly in the deep underground facility. In the reprocessing and recycle method, plutonium and uranium are recycled as fuels after the removal of FPs. Japan has a policy of reprocessing and recycle system to promote the efficient use of plutonium and uranium.

Figure 1-6 shows a schematic of the proposed nuclear fuel cycle system [14]. In Rokkasho village in Aomori prefecture, a nuclear reprocessing plant was built with a scale of is 800 t/y for fabrication of MOX (Mixed Oxide) fuels. In this system, spent nuclear fuels are sent to the back-end process which includes reprocessing, intermediate storage, MOX fuel fabrication, and disposal of the

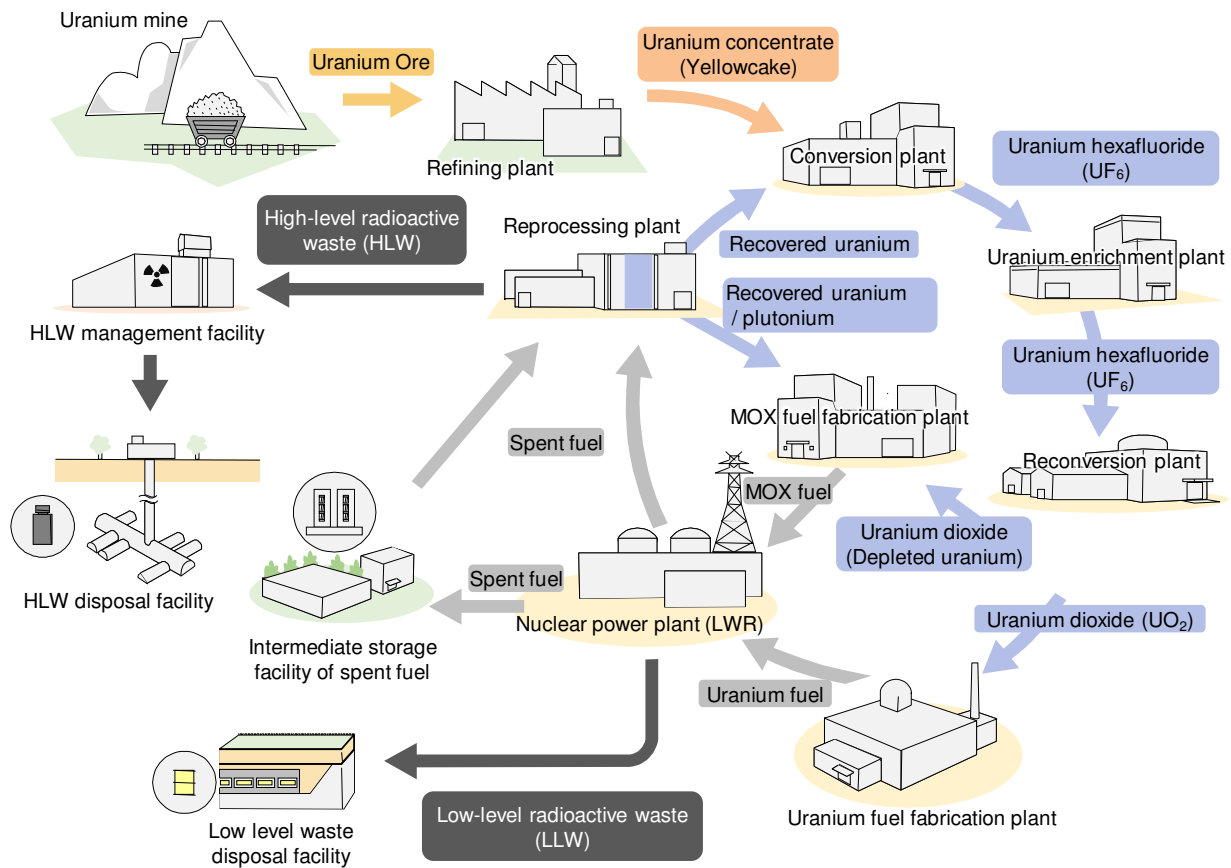


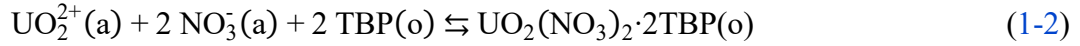
Figure 1-6 Schematic of nuclear fuel cycle in LWR [14].

wastes. In the reprocessing process, recovered uranium and plutonium are mixed and supplied as enriched MOX fuels with Pu 4–9% in LWR (Pu 15–30% for FBR). Most FPs are vitrified in glass as high level radioactive waste (HLW) and disposed in deep geological repository.

1.3 High-level radioactive waste

Figure 1-7 shows a flow chart of the reprocessing process called PUREX method. This name is an acronym standing for Plutonium Uranium and Redox EXtraction. After shearing spent fuel pins to be 3–5 cm length, fuel pellets are dissolved in nitric acid solution. Although most metals including FPs are completely dissolved in the dissolution process, several elements including Mo, Zr, Ru, Rh, and Pd remain as an insoluble residue. The insoluble residue is collected by a centrifugal clarifier and transferred to the vitrification process. Uranium and plutonium exist as hexavalent

(UO_2^{2+}) and tetravalent (Pu^{4+}) ions in the fuel solution, respectively. These ions are extracted in tributyl phosphate (TBP) which is diluted to be 20–30% by normal chain saturated hydrocarbon.



In this process, tetravalent and hexavalent actinide ions are also extracted by TBP. However, the pentavalent ions such as NpO_2^+ , and cations with valences equal or less than three, such as trivalent actinides of Am^{3+} and Cm^{3+} , and FPs, are difficult to extract. Residual liquid contains minor actinides (MAs) such as Am and Cm, and most FPs. This residual liquid is called as high level radioactive liquid waste (HLLW). After evaporation and condensation of HLLW, it is transferred to the vitrification process. The organic phase containing UO_2^{2+} and Pu^{4+} is transferred to the separation process.

In the separation process, Pu^{4+} is reduced to Pu^{3+} by adding reductant agent such as U^{4+} and hydroxylamine nitrate (HAN) to aqueous phase. Because Pu^{3+} is difficult to extract in TBP, plutonium in organic phase is transferred to aqueous phase. Recovered plutonium has many impurities such as Ru, Rh, and Np. On the other hand, uranium in organic phase is back-extracted to aqueous phase by diluted nitric acid. Recovered uranium contains mainly Np as an impurity. Crude uranium and plutonium are transferred to purification process. In purification process of plutonium, Pu^{3+} in aqueous phase is oxidized to Pu^{4+} by adding nitrous acid. Pu^{4+} is re-extracted by TBP and residual FPs are removed. Extracted Pu^{4+} is reduced and liquated by HAN again to aqueous phase as Pu^{3+} . In the purification process of uranium, the oxidation of Np from pentavalent to hexavalent is prevented by adding hydrazine. Since the extraction of the pentavalent Np in TBP is difficult, uranium is successfully separated and purified. Purified plutonium nitrate and uranyl nitrate are transferred to denitration process and recovered as oxides.

The fuel reprocessing of spent LWR fuels is operating in a commercial scale in four

countries: Japan, France, UK, and Russia. Typical PUREX process facilities are located in La Hague in France and Rokkasho in Japan. Active tests were conducted using real spent fuels in the Rokkasho reprocessing plant in September, 2012. The announced completion date of construction is in the first-half of 2018. HLW (HLLW and insoluble residue) generated in the reprocessing

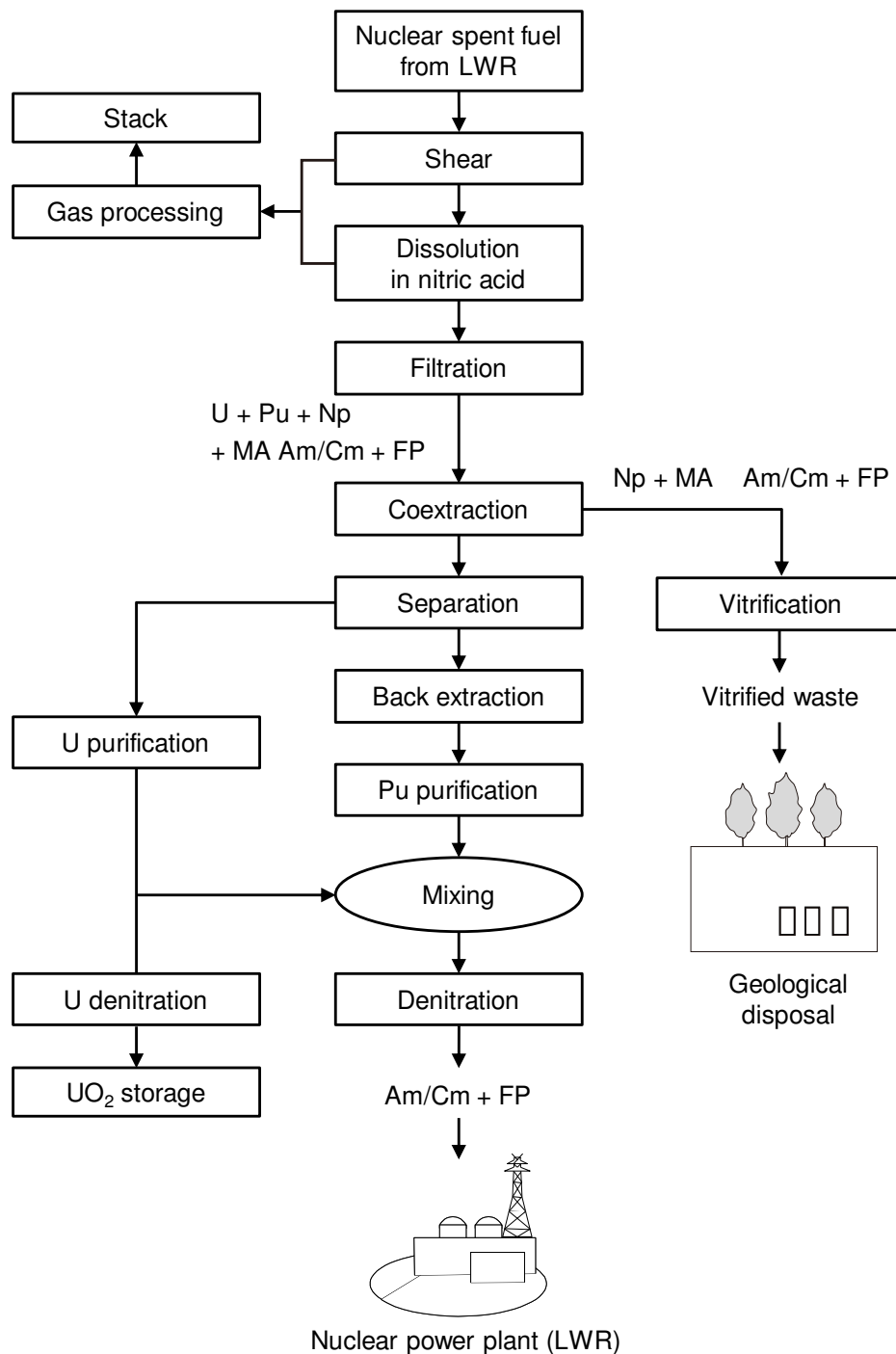


Figure 1-7 Flow chart of reprocessing process [10].

process is mixed with molten glass and vitrified by using melting furnaces. Vitrification plant is built with the reprocessing plant.

Figure 1-8 shows the change of radioactivity over time corresponding to 1 ton of 4.5 % low-enrichment uranium fuel [15]. The red dotted-lines shows the radioactivity for 750 ton of uranium ore which is needed to fabricate 1 ton of uranium fuel. The radioactivity of the fuel increases approximately 10 million times during the power generation. Through the spent fuel storage, the vitrified waste storage, and the geological disposal, radioactivity decays with time. The amount of radiation soon after fabrication in reprocessing plant reaches around 14,000 Sv near the canister, which is strong enough to bring crisis of death in a short period. Moreover, the temperature of the vitrified waste soon after fabrication is around 200 °C by the decay heat of radioactive elements. The radiation and temperature gradually decrease through storage period. The radiation decreases to one-several tenths and the temperature lowers to 100 °C after around 30 years from fabrication. However, the long-lived fission products (LLFPs) exist in the vitrified waste and these elements still continue to emit radioactive rays. At least tens of thousands years are necessary until the radioactivity becomes the same level as the uranium ore with negligible biological impact [15].

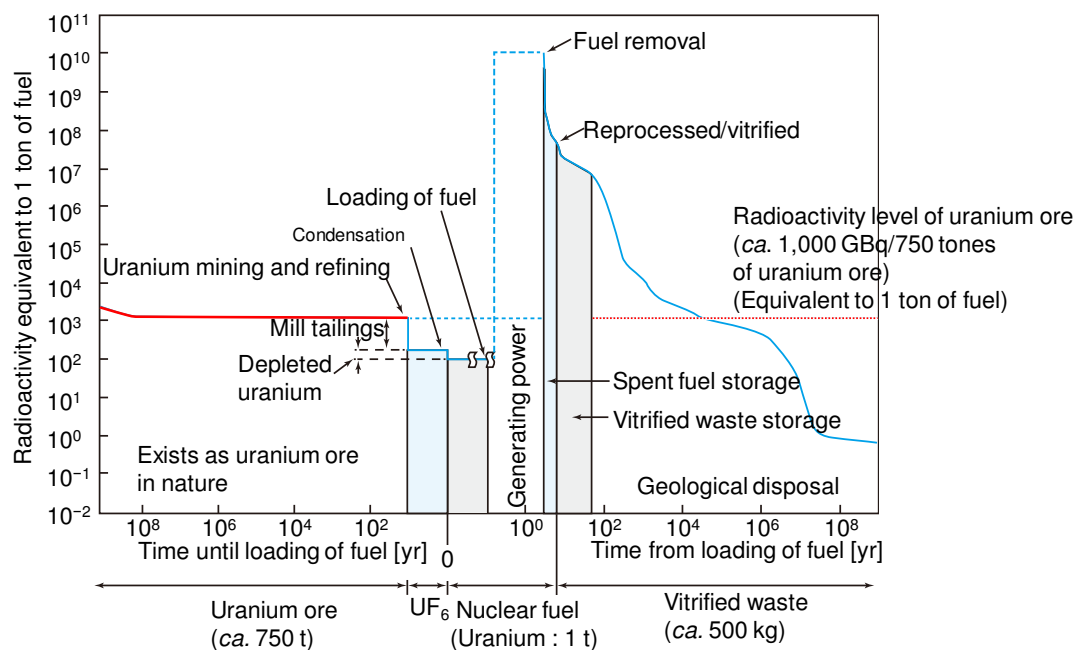


Figure 1-8 The change of radioactivity in 4.5 % low-enrichment uranium fuel of 1 ton over time [15].

1.4 Disposal methods of HLW

1.4.1 Geological disposal

Radioactive waste emits ionizing radiation which is harmful to humans and other creatures. In order to protect humans and other creatures from strong radioactivity of the vitrified wastes, the wastes need to be shielded or isolated from the biosphere. Japan has a policy of geological disposal for vitrified wastes. In the geological disposal, vitrified wastes are buried in deep geological depository for tens of thousands of years until the level of radioactivity decreases. Other disposal methods of HLW are explained in the next section.

Vitrified wastes fabricated in Japan are stored in stainless steel containers. The size of one vitrified waste is *ca.* 40 cm in diameter and 130 cm in height. Its volume and weight are *ca.* 150 L and 500 kg, respectively. Japan has around 17,000 tons of spent nuclear fuel in the storages and nuclear power plants. From the amount of spent fuel reprocessed in the past, Japan has the HLW corresponding to 25,000 pieces of vitrified waste from the spent nuclear fuel caused by nuclear power generation for a half century. One-year operation of a one-gigawatt-scale nuclear reactor requires *ca.* 30 tons of enriched uranium and generates 30 pieces of vitrified waste. Japan already has 50 nuclear reactors of one-gigawatt scale. When all the reactors are operated, 1,500 vitrified wastes are produced every year [16].

Currently, the construction of an underground facility with a capacity of more than 40,000 pieces of vitrified waste has been projected [17]. The planned facility is located at under 300 m depth from the ground with 6–10 km² area. [Figure 1-9](#) shows a schematic of the disposal of vitrified waste in multibarrier system. Vitrified waste is overpacked by a steel container with 20 cm thickness. Additionally, the compacted clay is solidified around the canister with 70 cm thickness and buried in bedrock deeper than 300 m from the ground. The bedrock also has a function to prevent from the leakage of radioactive waste. In Rokkasho, the vitrified wastes are stored in concrete building with air cooling. Recently, Japanese government has selected the candidate cites for the geological disposal. A map for the geological disposal is published based on

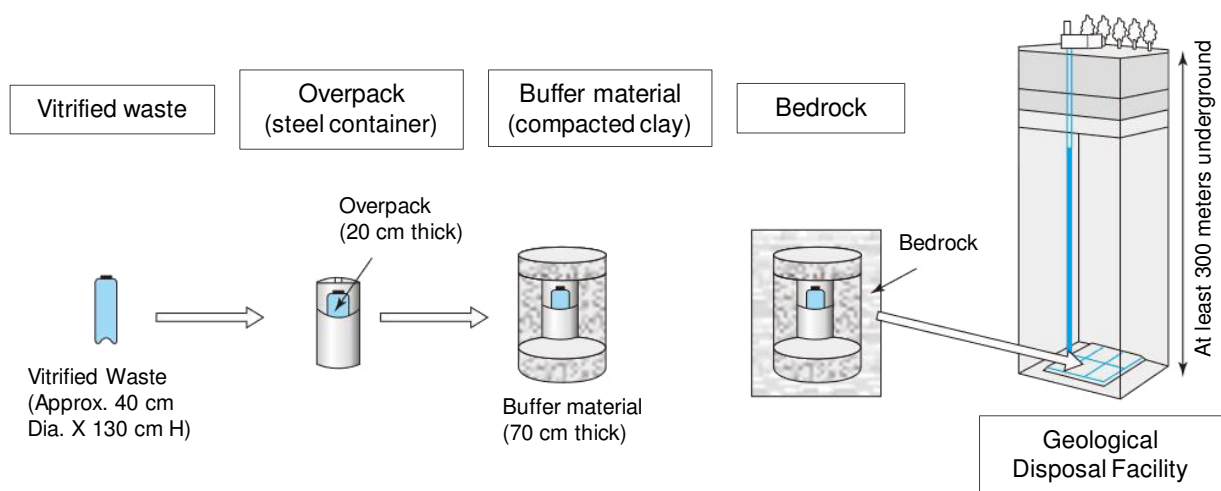


Figure 1-9 Schematic of disposal of vitrified waste in multibarrier system.

the stability of geological activities, and the possibility of damages by tsunami, volcanos, groundwater, and so on [18]. Although a large area is required to store the tremendous amounts of vitrified wastes, the selection of the appropriate sites for the geological disposal is difficult because there is no technology which can accurately forecast major earthquakes like the Great East Japan Earthquake and can estimate the risk of leakage of radioactive waste during tens of thousands of years.

1.4.2 Other disposal methods

Other disposal methods than the geological disposal are subduction zone disposal, ocean floor disposal, ice sheet disposal, and space disposal. The basic concept of these disposal methods is the same; radioactive wastes are physically kept far away from biosphere.

The subduction zone disposal was suggested by Fyfe *et al.* [19]. The geologists came up with this idea based on the plate tectonics theory presented in 1960s. In this disposal method, the radioactive wastes are supposed to be solid such as vitrified wastes. They would be discharged to deep subduction zones such as Japan Trench and Mariana Trench. Trenches are the deepest place on the earth where humans can access. In addition, since the subduction zone is the place where

one oceanic plate sinks into mantle, the wastes involved to the mantle cannot be put back to the sphere of human habitation. However, the realization of this disposal method is difficult because it violates the London Convention which regulates waste disposal in oceans.

In the ocean floor disposal method, wastes are disposed by a sedimentation on the ocean floor as shown in [Figure 1-10](#). Ocean sediments are homogeneously composed of small particles like clay minerals. Due to the quite low hydraulic gradient at the deep ocean floor, elements are moved not by advection but mainly by diffusion. Moreover, the ocean sediments can trap the radioactive materials and minimize the expansion of polluted area even in the case of a leakage of radioactive material. However, the London Convention is also an obstacle for the realization of this method.

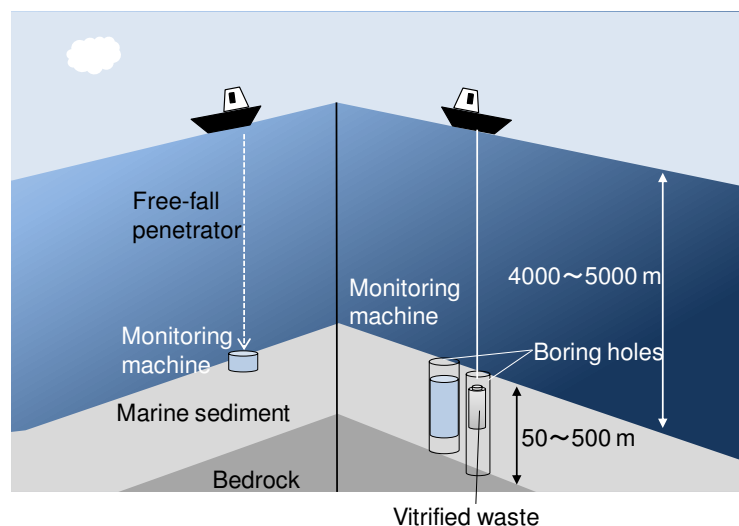


Figure 1-10 Schematic of the ocean floor disposal idea for radioactive waste.

The ice sheet disposal shown in [Figure 1-11](#) is a method to keep the waste in the ice sheet with a thickness of thousands of meters in Antarctic area. The idea was based on the knowledge that the Antarctic ice sheet has existed for hundreds of thousands of years. In this method, the heat produced from the vitrified waste is utilized for melting the ice sheet surrounding the vitrified waste. It gradually moves to the deeper part of the sheet and finally reaches the top of the bedrock. If the

ice sheet has been thick enough, the vitrified wastes are kept far from the biosphere. However, it is difficult to carry out this method because the Antarctic Treaty bans the disposal of radioactive waste. The possible global warming and climate change also require a consideration for the long-term use.

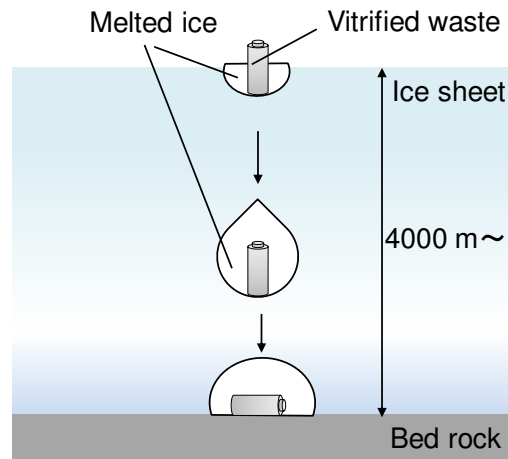


Figure 1-11 Schematic of the ice sheet disposal idea for radioactive waste.

The space disposal is a method to release the radioactive waste outside the earth, i.e., to the space as shown in [Figure 1-12](#). In this disposal, spacecrafts loading the radioactive wastes are launched and then operating a separation from the shuttle in the space. The problems are the cost and technical skills for launching the rocket, and worldwide serious pollution in the case of accident.

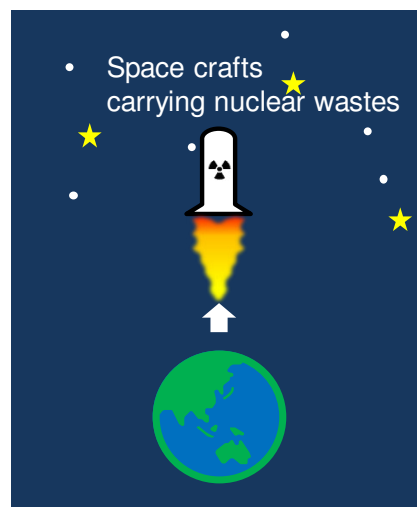


Figure 1-12 Schematic of the space disposal idea for radioactive waste.

1.4.3 Disposal of nuclear waste by nuclear transmutation

Among all possible disposal methods, the geological disposal is the only feasible solution [16]. One of the necessary technologies to realize the geological disposal is the reduction of the amount of the wastes. The idea aiming at decreasing the amount of radioactive wastes has been suggested: nuclear transmutation. A project was launched as OMEGA program since 1970s in Japan [20]. Here, the project was proceeded under the following concept. HLLW is firstly separated into 4 groups, minor actinides (MAs), platinum group, heat generating nuclides (^{99}Tc , ^{90}Sr , and ^{137}Cs), and other nuclides. Then, MAs are converted to short-lived nuclides by transmutation technique. Comprehensive studies were conducted by the development of accelerator-driven subcritical system (ADS). Nitrides of Pu and Zr were mainly studied due to advantages of stability of MAs and thermal conductivity.

Since 2015, another project was proposed for the reduction of nuclear wastes by using transmutation technique, which is one of the ImPACT programs (Impulsing Paradigm Change through Disruptive Technologies) [21]. In the proposal shown in Figure 1-13, LLFPs such as ^{135}Cs (half-life period: $t_{1/2} = 2.3$ million yr), ^{79}Se ($t_{1/2} = 0.295$ million yr), ^{107}Pd ($t_{1/2} = 6.5$ million yr), and ^{93}Zr ($t_{1/2} = 1.53$ million yr) are separately recovered from the vitrified wastes and spent nuclear fuels. After the recovery of LLFPs, they are converted to short-lived or stable nuclides. Owing to the recent technical development of accelerator and nuclear reaction knowledge, the exploration of the appropriate nuclear reaction is possible from both experimental and theoretical researches. The conversion of ^{107}Pd and other similar nuclides to stable and short-lived nuclides with a yield higher than 50 % was reported [22]. One simulation study shows that the γ -ray irradiation can succeed in conversion of ^{135}Cs to stable ^{134}Cs and short-lived nuclide ^{133}Cs with a yield higher than 90 % [23]. Conversion of ^{79}Se to ^{76}Se , ^{78}Se , ^{80}Se , and ^{82}Se [24] is also reported. A recent study shows that ^{93}Zr (half-life period: 1.53 million yr) was converted to stable nuclides with 39.1 % and short-lived nuclides (half-life period : ≤ 1 yr) with 56.8 % [25]. If this disposal process is established, not only a large amount of radioactive wastes will decrease, but some of the platinum group metals can

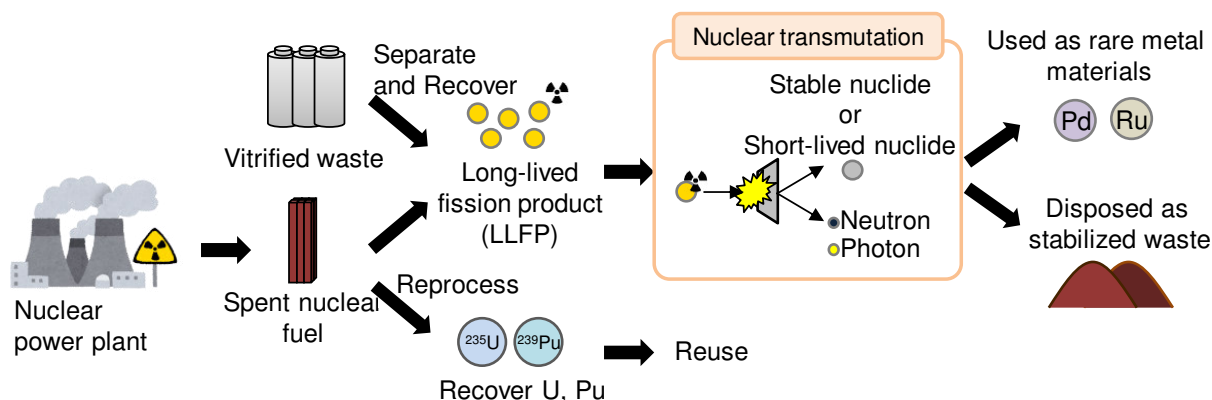


Figure 1-13 Flow chart of the disposal of radioactive nuclear waste by nuclear transmutation.

be utilized as catalysts for automobile and fuel cells.

To establish the process, the LLFPs have to be extracted from the vitrified wastes. Since the geological disposal has been considered as the only feasible way until the proposal of this project, no study on an extraction of LLFPs from the vitrified wastes has been conducted until very recently. The LLFPs are confined in the glass network structure as shown in Figure 1-14. To extract the LLFPs from vitrified waste, the decomposition of the Si–O network structure is required. A conventional method to decompose the glass network structure is the wet process using hydrofluoric acid. However, there are several drawbacks such as the use of a large amount of poisonous hydrofluoric acid, low processing rate, and a large amount of secondary wastes. Therefore, the development of process with higher reaction rate, decreased amount of secondary wastes, and avoidance of any poisonous chemicals is required.

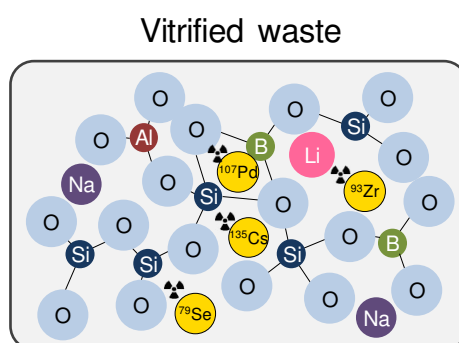
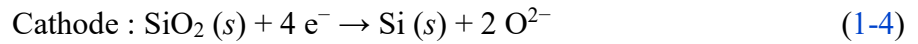


Figure 1-14 LLFPs confined in the glass network structure.

1.5 Electrochemical reduction of solid oxides in molten salts

Many studies have been conducted for electrochemical reduction of solid oxides in molten salts, especially for CaCl₂-based molten salts [26–61]. In 2000, Chen *et al.* firstly reported the electrochemical reduction of TiO₂ to Ti in molten salt [26]. Here, the TiO_x phase was formed on the surface, and then electron was supplied through TiO_x to reduce TiO₂ to Ti metal (Figure 1-15(a)). Nohira *et al.* reported the electrochemical reduction of solid SiO₂ to Si in molten CaCl₂ [27]. SiO₂ is known as an insulator even at high temperature and there exists no electroconductive SiO_x phase according to the phase diagram of the Si–O system. However, they showed that the electrochemical reduction of SiO₂ is possible. The reaction mechanism and the photos of the used electrodes are shown in Figure 1-15(b),(c) and Figure 1-16, respectively [61]. The electrochemical reduction of SiO₂ occurs at the three-phase interface among SiO₂, conductive metal, and molten salt.



Si produced by the reduction of SiO₂ also has a high conductivity at high temperature, which makes new electron paths. Since the produced Si layer is porous due to the volume shrinkage from SiO₂ to Si, molten salt penetrates into the gaps of the porous layer. As a result, a new three-phase interface of SiO₂/conductive Si/CaCl₂ is produced. The reduced area spreads from the initial three-phase interface with the progress of reduction. In the electrochemical reduction of SiO₂ in molten salt, the CaCl₂-based electrolytes were used because of the high solubility of O²⁻ ions [62]. Various groups have investigated the above reaction to apply to the production of solar-grade Si [28–46]. This reaction was also applied to the production of Si nanowires [47–49] and negative electrode materials of lithium ion battery [50].

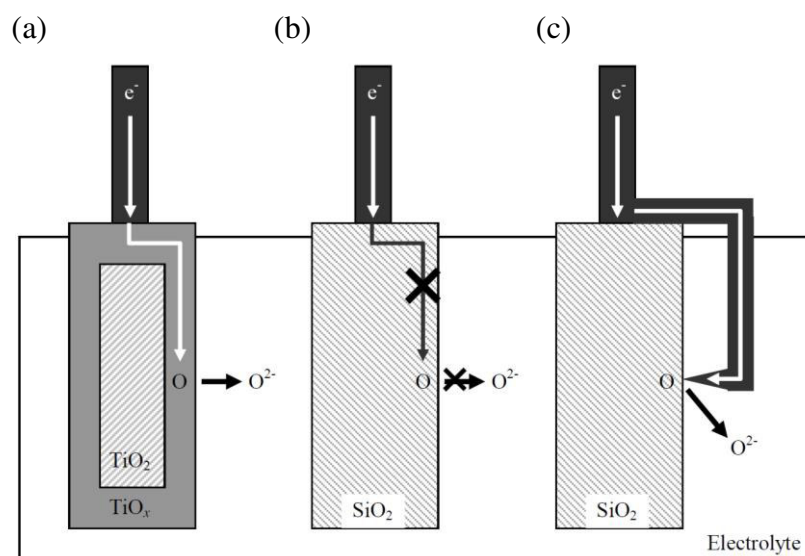


Figure 1-15 Mechanisms of the electrochemical reduction of (a) TiO_2 and (b), (c) SiO_2 in CaCl_2 [61].

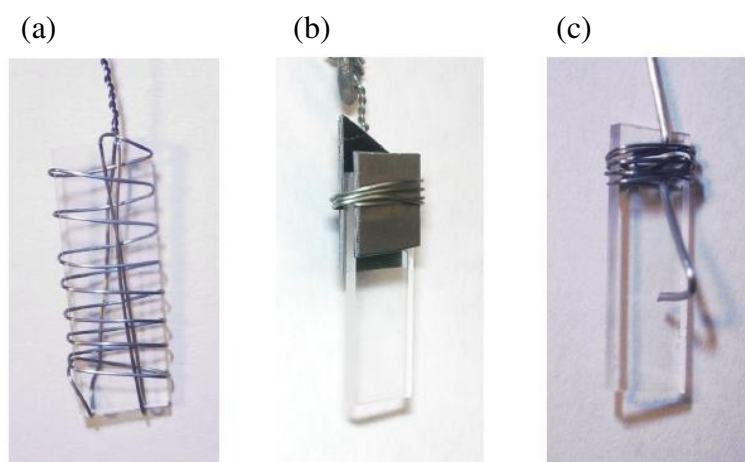


Figure 1-16 Photograph of the example of the contacting electrodes [61].

After the reports of electrochemical reduction of solid oxides such as TiO_2 and SiO_2 in molten CaCl_2 -based salts, electrochemical reductions of various oxides (Ti, Cr, Ce, Nb, Ta, W, Ni, Zr, Dy, and U) have been widely investigated in molten CaCl_2 -based salts [51,52]. Recently, in-situ analysis of electrochemical reduction of solid oxides was reported in high temperature molten salt for a clarification of the reduction mechanism [53–55]. The reductions of oxides mixtures (NiTiO_3 [53], $\text{TiO}_2+\text{SiO}_2$ [56,57], $\text{TiO}_2+\text{SiO}_2$ +other oxides [58], ZrSiO_4 [59], CaB_2O_4 [60], etc.)

have been also studied to develop a new production process of materials.

Moreover, the electrochemical reduction of spent oxide fuels has been studied by many research groups [63–71]. Sakamura *et al.* reported the electrochemical reduction of UO_2 in molten CaCl_2 or LiCl [63]. Hur *et al.* investigated the solubility of lanthanoid oxides under electrolytic reduction in molten $\text{LiCl-Li}_2\text{O}$ to form mixed oxides and electrochemical behavior of Br^- , I^- , and Se^{2-} in LiCl [68]. Yoo *et al.* reported the conceptual study of preprocessing for recovering actinoids from spent oxide fuels using the electrochemical reduction in molten LiCl [67].

1.6 Aims of this study

On the basis of knowledge of the reduction of SiO_2 in molten CaCl_2 , the author aimed to apply the electrochemical reduction of solid oxides in molten salts to the decomposition of Si–O network structure of the vitrified wastes. An establishment of a dry process with high reaction rate to decompose the Si–O network is expected. If the recovery of LLFPs from vitrified wastes and ongoing research of nuclear transmutation technique are combined, a large amount of vitrified waste can be decreased or utilized as precious metals.

Estimated composition of the vitrified waste glass is listed in Table 1-4. The largest component of vitrified wastes is SiO_2 (48.8 wt%). The second largest is B_2O_3 (14.8 wt%). Other main components are Na_2O (10.0 wt%), Al_2O_3 (5.2 wt%), CaO (3.1 wt%), Li_2O (3.1 wt%), and ZnO (3.1 wt%). The target LLFPs in this study are ZrO_2 (1.34 wt%), Cs_2O (0.68 wt%), PdO (0.40 wt%), and SeO_2 (0.02 wt%).

Table 1-4 **Estimated composition of the vitrified waste glass.**

Vitrified waste		
	Oxide	Composition / wt%
Base glass	SiO ₂	48.75
	B ₂ O ₃	14.79
	Na ₂ O	10.00
	Al ₂ O ₃	5.20
	CaO	3.09
	Li ₂ O	3.09
	ZnO	3.09
LLFP oxides	ZrO ₂	1.34
	Cs ₂ O	0.68
	PdO	0.40
	SeO ₂	0.02
FP oxides	CeO ₂	1.95
	MoO ₃	1.34
	Gd ₂ O ₃	1.26
	Nd ₂ O ₃	1.27
	RuO ₂	0.76
	BaO	0.53
	Pr ₆ O ₁₁	0.36
	MnO	0.32
	La ₂ O ₃	0.39
	SrO	0.26
	Sm ₂ O ₃	0.24
	Fe ₂ O ₃	0.16
	Y ₂ O ₃	0.16
	TeO ₂	0.16
	Rh ₂ O ₃	0.14
	Rb ₂ O	0.11
	SnO ₂	0.03
	Eu ₂ O ₃	0.04
Others	P ₂ O ₅	0.02
	Ag ₂ O	0.02
	NiO	0.02
	Cr ₂ O ₃	0.01
Actinide oxides	UO ₂	small
	PuO ₂	
	NpO ₂ etc.	

Predicted behaviors of the LLFPs in the whole processes are shown in [Figure 1-17](#). The behaviors during electrochemical reduction of the vitrified waste are supposed to be different among the elements. Some elements will remain in the solid phase as Si alloys or oxides. For example, Pd is likely to form alloys with Si, and Zr is supposed to stay as the oxides. Cs and Se are considered to dissolve into molten salt. The LLFP elements are further separated by various

methods including molten salt electrolysis. Since the actual behaviors of constituent elements, especially for LLFPs, have not been clarified, they are to be investigated in this study through the experiments on electrochemical reduction of vitrified wastes in molten CaCl_2 .

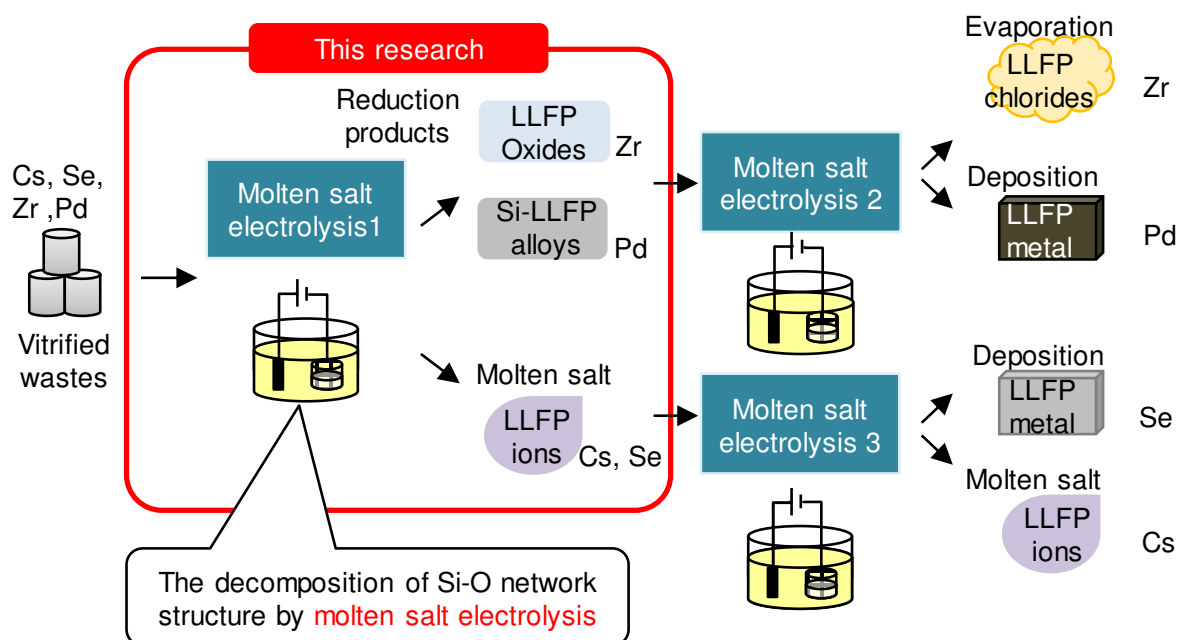


Figure 1-17 Supposed process for the recovery of LLFPs from the vitrified wastes by electrochemical reduction in molten salt.

1.7 Overview of this study

In this study, the electrochemical reduction of vitrified nuclear wastes in molten CaCl_2 is investigated for an establishment of a technique to recover LLFPs from the vitrified wastes. As mentioned in the previous section, complicated reduction behaviors are anticipated because the vitrified nuclear wastes are composed of many oxides. Therefore, the reduction behavior of several simplified glass was investigated as separated stages. As the first stage, the simplest glass (Pyrex[®] glass and Tempax[®] glass) is investigated. Then, electrochemical reduction behavior is investigated by increasing the number of oxides step by step. In the final stage, the vitrified waste simulant with the stable isotopes of FPs is investigated. [Table 1-5](#) summarizes the compositions of the vitrified

wastes glass (estimated), Pyrex[®] glass, simulants 1, 2, and 3. Simulant 1 is composed of only base glass components. Simulant 2 includes LLFP oxides in the glass with the same component of simulant 1. Simulant 3 has almost the same composition with the typical vitrified wastes using stable isotopes as components and containing Ce as a simulated element of U. Table 1-6 shows target and analyzed compositions of simulant 3 used in this study.

In Chapter 2, the behaviors of elements contained in the vitrified wastes are predicted from the thermodynamic calculations. Ellingham diagrams and potential- pO^{2-} diagrams of the elements related to the reactions are constructed. All the elements listed in Table 1-6, which are contained in simulant 3, have been calculated.

In Chapter 3, the electrochemical reduction behaviors of borosilicate glass in molten $CaCl_2$ were investigated by using Pyrex[®] glass. This is because the borosilicate glass has a similar composition as the vitrified wastes and small number of components. The electrochemical reduction behaviors are investigated by cyclic voltammetry and analysis of the samples obtained by the potentiostatic electrolysis of the glass-seal electrodes of borosilicate glass and silica glass. In addition, potentiostatic electrolysis of a large amount of borosilicate and silica glass plates is conducted. The obtained samples are analyzed for more detailed characterization of the products.

In Chapter 4, electrochemical reduction behavior of Al_2O_3 is investigated. Al_2O_3 is the fourth largest component in the vitrified wastes, following SiO_2 , B_2O_3 , and Na_2O . The reduction behaviors are discussed from the results of potentiostatic electrolysis of Al_2O_3 powder in molten $CaCl_2$ at various potentials. Then, the reduction of an Al_2O_3 tube is carried out by using the improved electrode structure to enhance the diffusion of O^{2-} ions.

In Chapter 5, electrochemical reduction is conducted for the powder of simulant 1 which is composed of SiO_2 , B_2O_3 , Al_2O_3 , Li_2O , CaO , and ZnO . The reduction products obtained by the potentiostatic electrolysis at various potentials are analyzed. Moreover, electrochemical reduction is investigated for simulant 2 which consists of the same component of simulant 1 and LLFP oxides of ZrO_2 , PdO , Cs_2O , and SeO_2 . The behavior of the elements especially for four LLFPs during the

electrochemical reduction of simulant 2 is studied by ICP-AES/MS for the reduction products and sampled molten salt. The behavior is also discussed based on the potential– pO^{2-} diagrams.

In Chapter 6, the electrochemical reduction of simulant 3 is investigated. Since simulant 3 has almost the same composition as the actual vitrified waste, the number of oxides to be studied is as many as 33. In the first experiment, simulant 3 is reduced by small crucible electrodes to evaluate the reduction rate and explore the behavior of the elements. In other experiments, tens of grams of simulant 3 is reduced by using a large graphite crucible electrode to obtain the knowledge of the behavior in large scale electrolysis, which is useful for the practical application.

Finally, Chapter 7 summarizes the behavior of each element during the electrolysis of the vitrified wastes, and discusses the establishment of the recovery process of LLFPs from the vitrified wastes.

Table 1-5 Composition of Pyrex[®] glass, simulants 1, 2, and 3.

	Pyrex [®] glass	Simulant 1	Simulant 2	Simulant 3
Electrochemical				
reduction in	Chapter 3	Chapter 5	Chapter 5	Chapter 6
molten salt				
Softening point	1093 K	863 K	873 K	873 K (estimated)
Composition				
/ wt%				
SiO ₂	80.8	55.4	53.7	48.8
B ₂ O ₃	12.6	16.8	16.3	14.8
Na ₂ O	4.0	11.4	11.1	10.0
K ₂ O	0.4	-	-	-
Al ₂ O ₃	2.3	5.9	5.7	5.2
CaO	-	3.5	3.4	3.1
Li ₂ O	-	3.5	3.4	3.1
ZnO	-	3.5	3.4	3.1
			ZrO ₂	1.5 ZrO ₂
			Cs ₂ O	1.0 Cs ₂ O
LLFP oxides	-	-	PdO	0.5 PdO
			SeO ₂	0.1 SeO ₂
Other FP oxides	-	-	-	9.34
Others	-	-	-	0.3

- : Not included

Table 1-6

Target and analyzed compositions of simulant 3 used in this study.

Composition / wt%			
	Component	Target	Analyzed
Base glass	SiO ₂	48.75	50.5
	B ₂ O ₃	14.79	13.6
	Na ₂ O	10.00	9.24
	Al ₂ O ₃	5.20	5.47
	CaO	3.09	3.08
	Li ₂ O	3.09	3.06
	ZnO	3.09	3.21
LLFP oxides	ZrO ₂	1.34	1.31
	Cs ₂ O	0.68	0.71
	PdO	0.40	0.37
	SeO ₂	0.02	0.02
FP oxides	CeO ₂	1.95	1.94
	MoO ₃	1.34	1.36
	Gd ₂ O ₃	1.26	1.24
	Nd ₂ O ₃	1.27	1.09
	RuO ₂	0.76	0.70
	BaO	0.53	0.54
	Pr ₆ O ₁₁	0.36	0.35
	MnO	0.32	0.34
	La ₂ O ₃	0.39	0.33
	SrO	0.26	0.27
	Sm ₂ O ₃	0.24	0.21
	Fe ₂ O ₃	0.16	0.21
	Y ₂ O ₃	0.16	0.17
	TeO ₂	0.16	0.13
	Rh ₂ O ₃	0.14	0.12
	Rb ₂ O	0.11	0.11
	SnO ₂	0.03	0.03
	Eu ₂ O ₃	0.04	0.03
Others	P ₂ O ₅	0.02	0.03
	Ag ₂ O	0.02	0.02
	NiO	0.02	0.02
	Cr ₂ O ₃	0.01	0.01

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Chapter 2

Thermodynamic calculations

2.1 Introduction

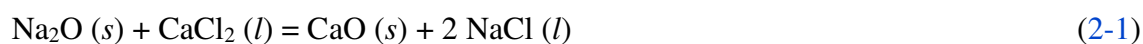
The electrochemical reduction behavior of nuclear waste simulant is predicted from the thermodynamic calculations. In this chapter, Ellingham diagrams are plotted and potential– $p\text{O}_2$ diagrams are constructed from thermodynamic data to predict the behaviors of each element in molten CaCl_2 at 1123 K. The behavior such as the dissolution into molten salt or remaining in the solid phase is discussed. In addition, the stable region and the reduction potential of the compounds are discussed. Most of the thermochemical data were taken from HSC Chemistry 6.1 (Outotec). Herein, the used thermodynamic calculation temperature is 1123 K, though some of the experimental temperature was 1103 K to prevent the softening of the glass.

2.2 Ellingham diagrams

Prior to the experiments, the reactions were estimated by Ellingham diagrams for oxides and chlorides. [Figure 2-1\(a\)](#) shows the Ellingham diagram for the oxides in the reaction system (MO_x , $M=\text{Si}$, B , Al , Na , K , and Ca , the components of borosilicate glass). Among the components of borosilicate glass, K_2O , Na_2O , and B_2O_3 are less stable than SiO_2 . Although the stability of oxides in the complex oxide may be somewhat different from that of the pure oxides, these oxides are expected to be reduced at more positive potentials than the reduction potential of SiO_2 (1.25 V [\[1\]](#)). On the other hand, the diagram shows that the reduction of Al_2O_3 proceeds at a more negative potential. In the case of pure Al_2O_3 , the formation of calcium aluminate depended on the

conditions.[2]

Figure 2-1(b) shows the Ellingham diagram for the related chlorides (MCl_x , $M=Si, B, Al, Na, K$, and Ca) [3]. While the Gibbs energies of formation for Na_2O and K_2O are far more positive than that of CaO , those for $NaCl$ and KCl are as negative as that for $CaCl_2$. Thus, as outlined below by Equations 2-1 and 2-2, the reaction of Na_2O or K_2O with molten $CaCl_2$ is thermodynamically favorable.

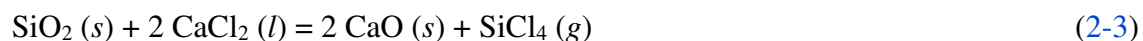


$$\Delta G^\circ_{1123K} = -246.5 \text{ kJ mol}^{-1} \text{ (Ref. [3])}$$

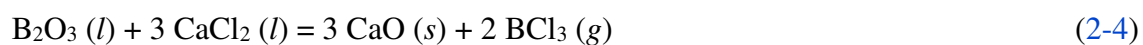


$$\Delta G^\circ_{1123K} = -347.7 \text{ kJ mol}^{-1} \text{ (Ref. [3])}$$

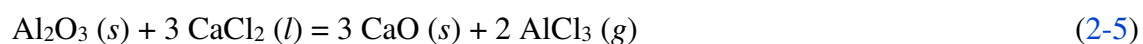
Namely, the components of Na_2O and K_2O in the glass are expected to dissolve to molten salt as $NaCl$ and KCl . On the contrary, for SiO_2 , B_2O_3 , and Al_2O_3 , the reactions with molten $CaCl_2$ are unfavorable, as seen below in Equations 2-3, 2-4, and 2-5.



$$\Delta G^\circ_{1123K} = 409.5 \text{ kJ mol}^{-1} \text{ (Ref. [3])}$$



$$\Delta G^\circ_{1123K} = 623.2 \text{ kJ mol}^{-1} \text{ (Ref. [3])}$$



$$\Delta G^\circ_{1123K} = 666.2 \text{ kJ mol}^{-1} \text{ (Ref. [3])}$$

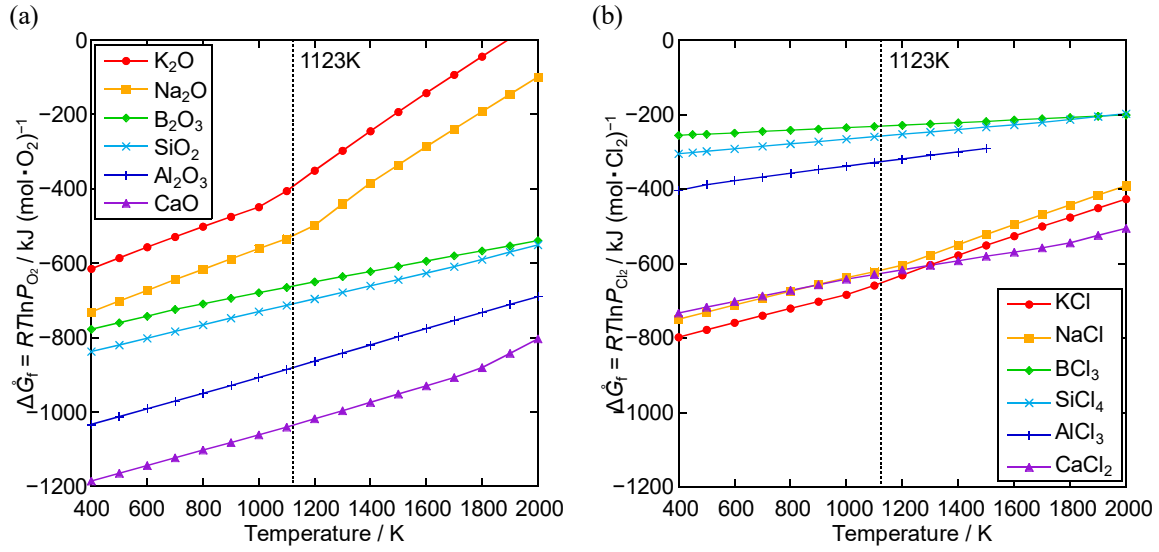


Figure 2-1 Ellingham diagrams for selected (a) oxides and (b) chlorides

Ellingham diagram is generally used to predict the stability of compounds. The dissolution behavior of the constituent oxides in molten CaCl_2 without electrolysis at 1123 K was thermodynamically discussed. Figure 2-2 plots the standard Gibbs energies of formation of oxides in vertical axis and those of chlorides in horizontal axis. The standard Gibbs energy of dissolution reaction (2-6), $\Delta G_{(\text{Dis_CaCl}_2)}^\circ$, is calculated by Equation 2-7.



$$\Delta G_{(\text{Dis_CaCl}_2)}^\circ = \left(\frac{1}{x} \Delta G_f^\circ(\text{MCl}_2) + \Delta G_f^\circ(\text{CaO}) \right) - \left(\frac{1}{x} \Delta G_f^\circ(\text{MO}_x) + \Delta G_f^\circ(\text{CaCl}_2) \right) \quad (2-7)$$

The orange line in Figure 2-2 corresponds to the zero value of $\Delta G_{(\text{Dis_CaCl}_2)}^\circ$. The elements in yellow region (Rb, Cs, Na, Li, Ba, Ag, and Sr) are favorable to dissolve into molten CaCl_2 owing to the negative value of $\Delta G_{(\text{Dis_CaCl}_2)}^\circ$. Since Ag_2O has the positive standard Gibbs energy of formation, Ag_2O is unstable at 1123 K. It will decompose into metallic Ag and O_2 gas. Several elements in blue region (Zn, Mn, La, Pr, and Ce) close to the orange line might partially dissolve into molten salt. Other elements which locate well below the orange line will not dissolve in molten

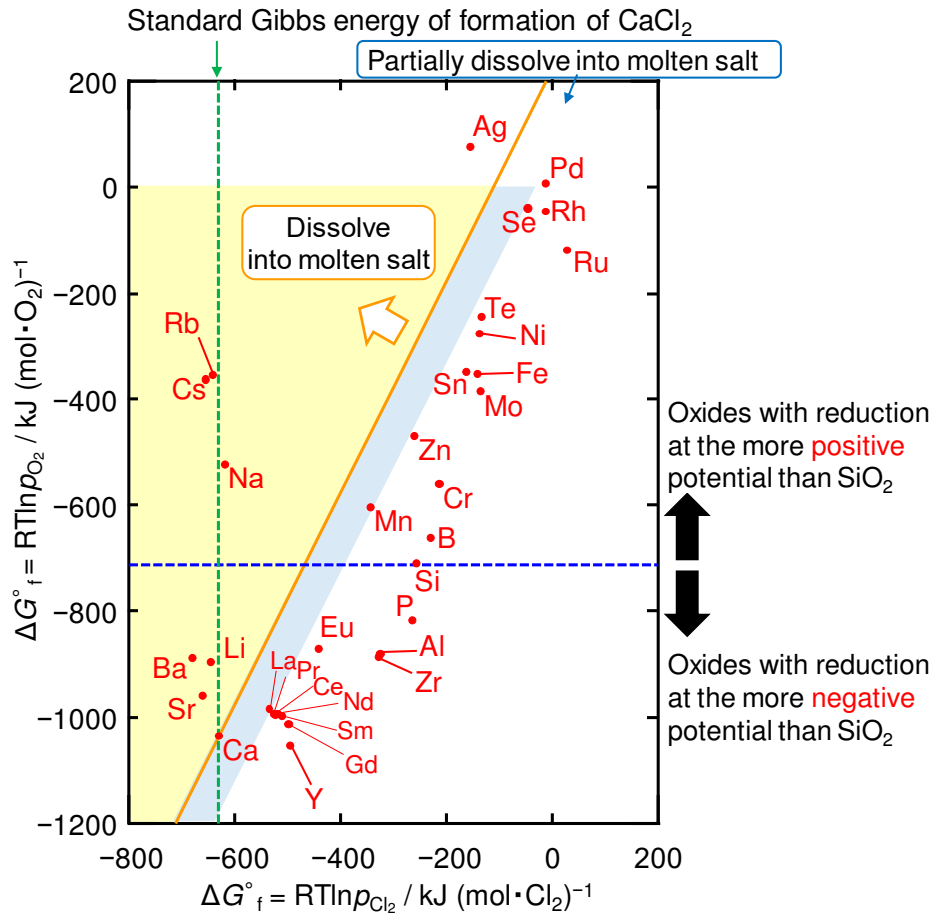


Figure 2-2 Plot of the standard Gibbs energy of formation of oxides and chlorides for the elements contained in the simulant 3. The oxidation state are indicated with asterisk (*) marks in Table 2-2.

CaCl₂ when they are just immersed in the molten salt.

2.3 Potential– pO^{2-} diagrams

In order to predict the electrolysis products of simulant 3, the potential– pO^{2-} diagrams were constructed for various M–Ca–O–Cl systems in molten CaCl₂ at 1123 K, where M = Si, B, Al, Na, K, Li, Zn, Zr, Cs, Pd, Se, U, Rb, Sr, Ba, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ru, Rh, Ag, P, Sn, Te, Cr, Mn, Fe, Ni, and Mo. Littlewood [4] and several researchers [2,4–20] constructed the potential– pO^{2-} diagrams to understand the electrochemical reactions in molten salts. The thermodynamic data used for this study are listed in Table 2-2 (in Section 2.5). The electrochemical

window of CaCl_2 was calculated to be 3.26 V from the standard Gibbs energy of formation of $\text{CaCl}_2(l)$. The chemical potential of $\text{CaO}(l)$ was determined to be $-496.9 \text{ kJ mol}^{-1}$ from the solubility of CaO in molten CaCl_2 and the thermodynamic data for $\text{CaO}(s)$ [17]. The evolution potential of 1 atm O_2 gas changes with $p\text{O}^{2-}$ value, as indicated in Equation 2-8.

$$E_{\text{O}_2/\text{O}^{2-}} = 2.575 + 0.111 p\text{O}^{2-} \quad (2-8)$$

The frames of the potential– $p\text{O}^{2-}$ diagrams for CaCl_2 at 1123 K are drawn by the dotted lines in following all potential– $p\text{O}^{2-}$ diagrams.

2.3.1 Si–Ca–O–Cl system

Figure 2-3(a) shows the potential– $p\text{O}^{2-}$ diagram for the Si–Ca–O–Cl system in molten CaCl_2 at 1123 K. The diagram was drawn on the basis of the one reported in previous paper [17], but the thermodynamic data for Si–Ca alloys, which were reported by Toba *et al.* [21], are added. CaSiO_3 phase is found to be stable at $4.49 < p\text{O}^{2-} < 5.18$ in the melt. At positive potentials and high CaO concentrations (i.e., low $p\text{O}^{2-}$ values), other calcium silicate compounds are stable. The

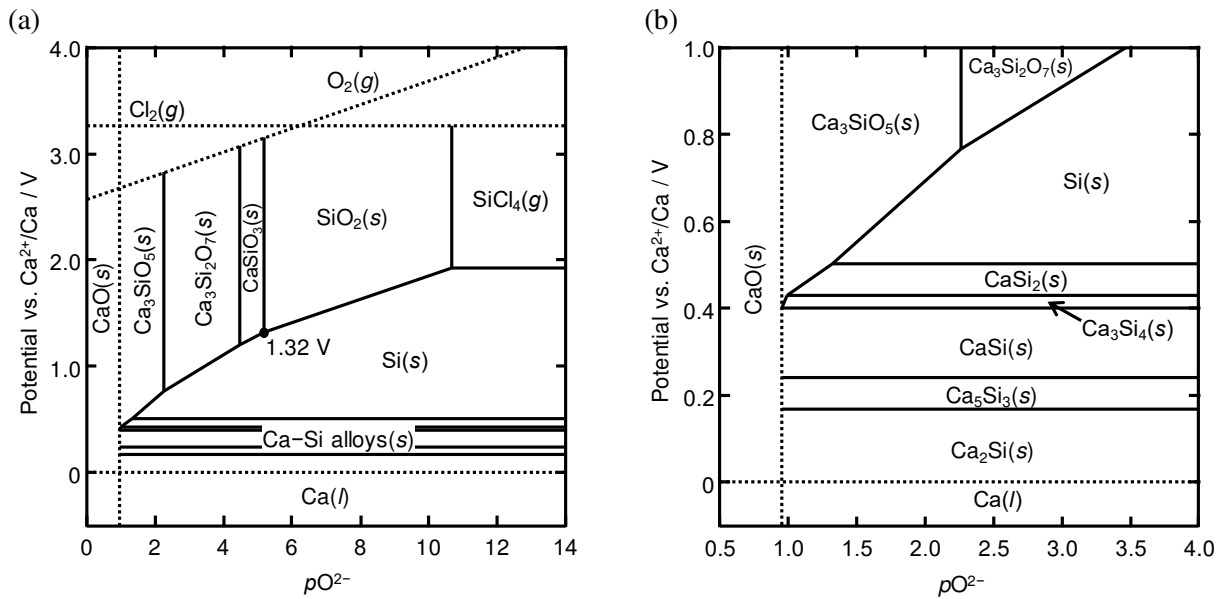


Figure 2-3 Potential– $p\text{O}^{2-}$ diagrams for the Si–Ca–O–Cl system in molten CaCl_2 at 1123 K for the (a) whole region and (b) low $p\text{O}^{2-}$ region.

potential at the three-phase boundary for $\text{SiO}_2/\text{CaSiO}_3/\text{Si}$ is calculated to be 1.32 V vs. Ca^{2+}/Ca , which has been reported to be the initial reduction potential of SiO_2 . Figure 2-3(b) shows the potential- $p\text{O}^{2-}$ diagram in the low $p\text{O}^{2-}$ and negative potential region, and indicates the formation of Si-Ca alloys. Five Si-Ca alloys are found at 1123 K. Since the equilibrium potential between Si and $\text{CaSi}_2(s)$ is 0.50 V, the Si-Ca alloys form at a more negative potential.

2.3.2 B-Ca-O-Cl system

The potential- $p\text{O}^{2-}$ diagram for the B-Ca-O-Cl system is shown in Figure 2-4. At $6.02 < p\text{O}^{2-} < 6.43$, CaB_4O_7 phase is formed in the melt. The potential of 1.58 V at the three-phase boundary of $\text{B}_2\text{O}_3/\text{CaB}_4\text{O}_7/\text{B}$ is more positive than the corresponding value for the Si-Ca-O-Cl system (1.32 V). The boundary between B_2O_3 or calcium borates and elemental B is more positive than that between SiO_2 or calcium silicates and elemental Si, as indicated with the red dashed line in Figure 2-4. Since the activity of $\text{B}_2\text{O}_3(l)$ is less than unity in the glass network, the stable region of B_2O_3 should be larger than that in Figure 2-4. The formation potential of CaB_6 from elemental B is 0.46 V. The calcium borates do not equilibrate with the CaB_6 phase because the elemental B phase is located between them (Figure 2-4). There is a discrepancy in the experimental report by Yin *et al.* in which CaB_6 was formed without elemental B during the reduction of CaB_2O_4 in CaCl_2 at 973 K [22].

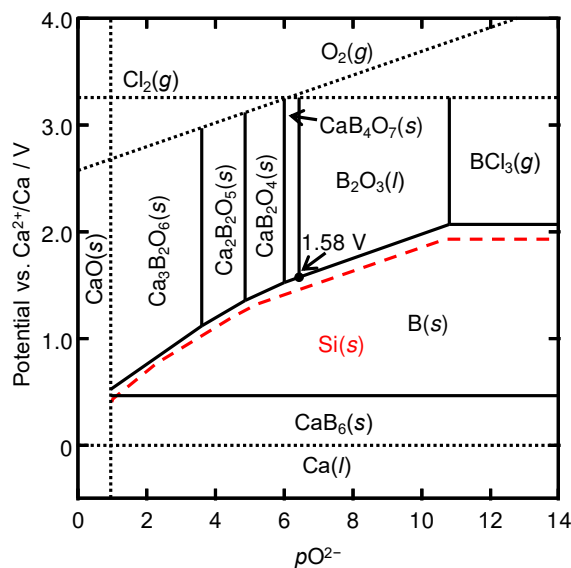


Figure 2-4 Potential- pO^{2-} diagram for the B-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

2.3.3 Al-Ca-O-Cl system

Figure 2-5 shows the potential- pO^{2-} diagram for the Al-Ca-O-Cl system. Unlike the B-Ca-O-Cl system, the boundary between Al_2O_3 or calcium aluminates and Al metal is more negative than that between SiO_2 or calcium silicates and elemental Si, as indicated by the red dashed line in Figure 2-5(a). The potential of 0.78 V at the three-phase boundary of $Al_2O_3/CaAl_{12}O_{19}/Al$ is more negative than that for $SiO_2/CaSiO_3/Si$ in the Si-Ca-O-Cl system (1.32 V). The formation potential of Al_2Ca alloy is found to be 0.36 V. In the potential- pO^{2-} diagram for Al-Ca-O-Cl in molten $CaCl_2$ -NaCl reported by Yan *et al.* [2], the stable region of for Al_2Ca was larger than that in Figure 2-5(a).

According to the phase diagram of the Al-Ca system [23] shown in Figure 2-6, the stable phases at 1123 K are Al-rich Al-Ca liquid alloy, solid Al_2Ca , and Ca-rich Al-Ca liquid alloy. Here, the Ca content, x_{Ca} , in the Al-rich Al-Ca liquid alloy that equilibrates with Al_2Ca is 0.16. Because the activity of Ca was reported to be 1.7×10^{-3} at this composition at 1373 K [24], the activity coefficient, γ_{Ca} , and electrode potential, E , in the {Al-rich Al-Ca (*l*) and Al_2Ca (*s*)} two-phase state at 1123 K are calculated to be:

$$\gamma_{\text{Ca}} (x_{\text{Ca}} = 0.16) = 3.85 \times 10^{-3} \quad (2-9)$$

$$E (\text{Al-rich Al-Ca } (l)/\text{Al}_2\text{Ca } (s)) = 0.357 \text{ V vs. Ca}^{2+}/\text{Ca} \quad (2-10)$$

Here, the interaction parameter, Ω , is assumed to be independent of temperature ($\Omega = RT \ln \gamma = \text{const.} \therefore T \ln \gamma = \text{const.}$), where R and T are the gas constant and the absolute temperature, respectively. In the same manner, the electrode potential in the {Ca-rich Al-Ca (l) and Al_2Ca (s)} two-phase state at 1123 K is estimated from the reported activity of Ca, 0.313, at 1619 K [25].

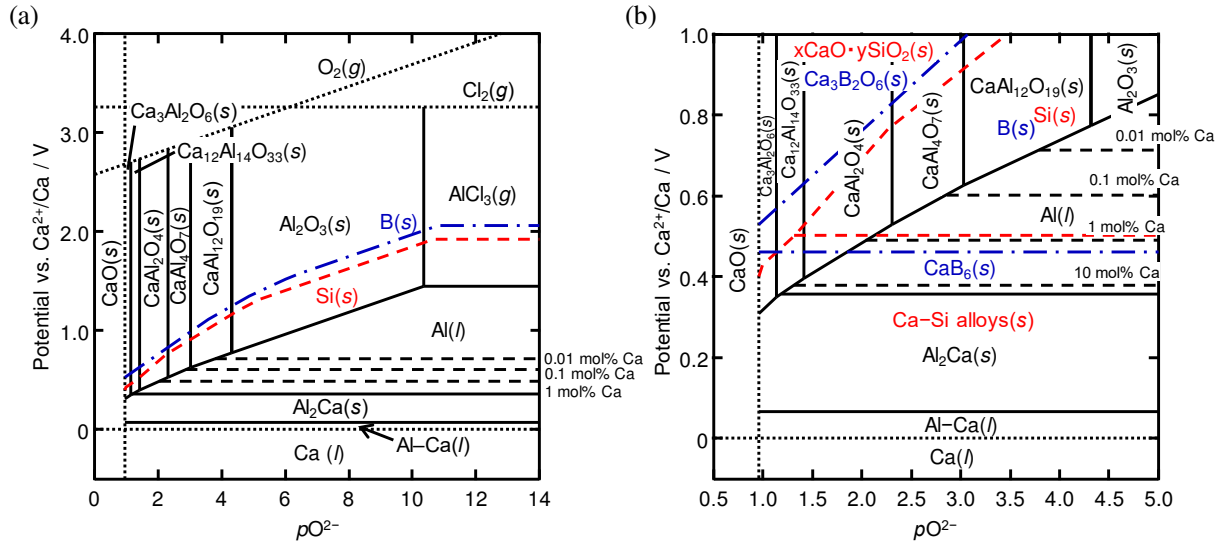


Figure 2-5 Potential- $p\text{O}^{2-}$ diagrams for the Al-Ca-O-Cl system in molten CaCl_2 at 1123 K for the (a) whole region and (b) low $p\text{O}^{2-}$ region (red dashed line: boundary between Si and other compounds in Si-Ca-O-Cl system, blue dash-dot line: boundary between B and other compounds in B-Ca-O-Cl system).

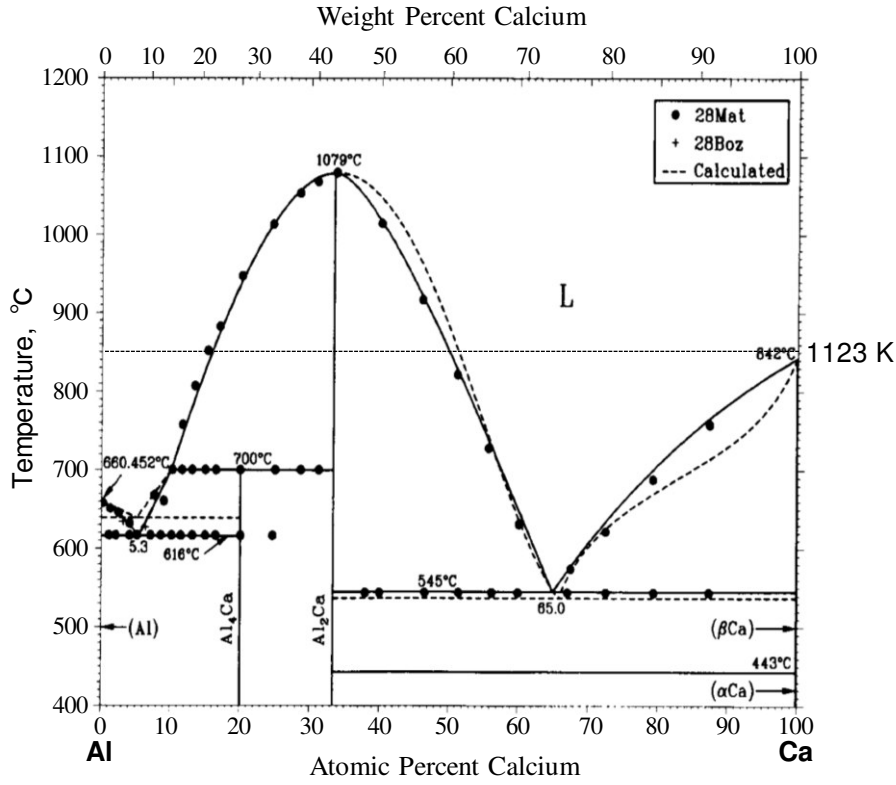


Figure 2-6 Phase diagram for the Al–Ca system [23].

$$E (\text{Ca-rich-Al-Ca } (l)/\text{Al}_2\text{Ca}(s)) = 0.067 \text{ V vs. Ca}^{2+}/\text{Ca} \quad (2-11)$$

Based on the above calculations, the stable regions in the potential– $p\text{O}^{2-}$ diagram are determined for Al-rich Al–Ca alloy (l), Al_2Ca (s), and Ca-rich Al–Ca alloy (l). There is a wide stable region of liquid Al in the high– $p\text{O}^{2-}$ region, *i.e.*, low activity of O^{2-} ions. Here, the content of Ca in the liquid Al is determined by the electrode potential. The potential values corresponding to several representative Ca contents in the liquid Al are plotted with dashed lines in Figure 2-5(a) and (b). Al_2Ca is predicted to be formed at potentials more negative than 0.36 V. Ca-rich Al–Ca(l) alloy forms at potentials more negative than 0.067 V. When the thermodynamic data obtained by FP-CALPHAD method [26] is adopted, the potentials of Al_2Ca formation and Ca-rich Al–Ca(l) alloy formation are calculated as 0.310 V and 0.101 V, respectively. The potential at the three-phase equilibrium between $\text{CaAl}_{12}\text{O}_{19}$, Al, and Al_2O_3 is 0.78 V, $p\text{O}^{2-} = 4.31$. A total of five stable regions

for calcium aluminates appear in the low- pO^{2-} range: $CaAl_{12}O_{19}$ ($3.04 \leq pO^{2-} \leq 4.31$, $E \geq 0.62$ V), $CaAl_4O_7$ ($2.31 \leq pO^{2-} \leq 3.04$, $E \geq 0.53$ V), $CaAl_2O_4$ ($1.41 \leq pO^{2-} \leq 2.31$, $E \geq 0.40$ V), $CaAl_4O_7$ ($1.16 \leq pO^{2-} \leq 1.41$, $E \geq 0.35$ V), and $Ca_{12}Al_{14}O_{33}$ ($1.08 \leq pO^{2-} \leq 1.16$, $E \geq 0.34$ V). It should be noted that $Ca_{12}Al_{14}O_{33}$ did not appear in the Al–Ca–O phase diagram at 1273 K published in 1990 [27], because its thermodynamic data was reported recently.

2.3.4 Na and K–Ca–O–Cl system

The potential- pO^{2-} diagrams for the Na–Ca–O–Cl and K–Ca–O–Cl systems are shown in Figure 2-7(a) and (b), respectively. The stable phases are NaCl(*l*) and Na(*l*) in Figure 2-7(a) and KCl(*l*) in Figure 2-7(b). The dashed line in Figure 2-7(b) shows the formation potential of K(*g*) calculated from the decomposition voltage of KCl(*l*). The diagrams also suggest that both Na₂O and K₂O are thermodynamically favorable to dissolve in the melt.

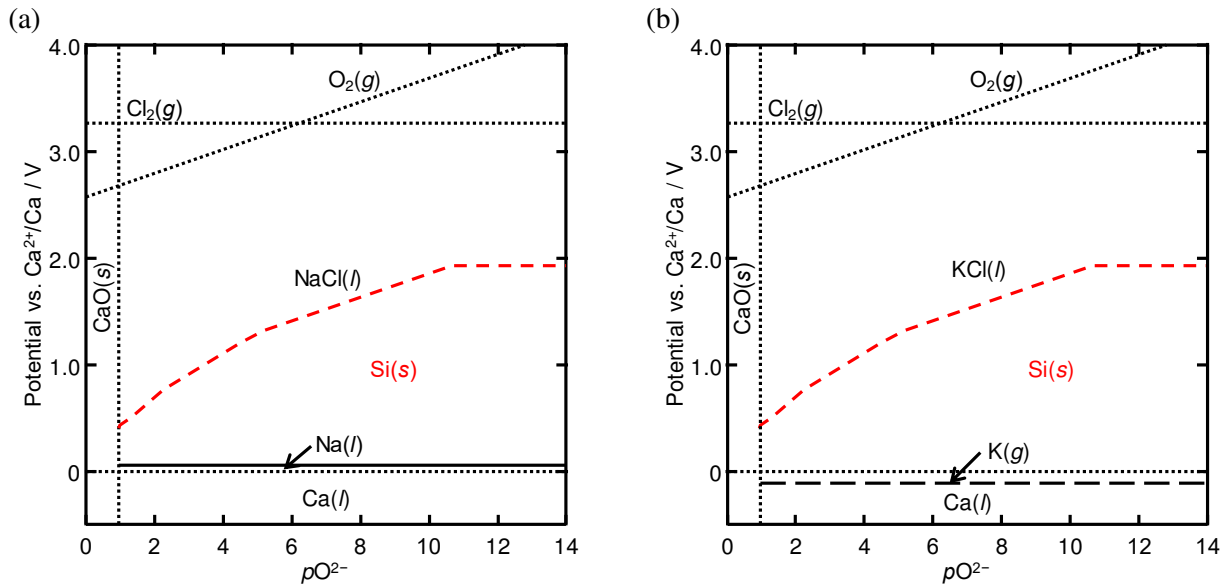
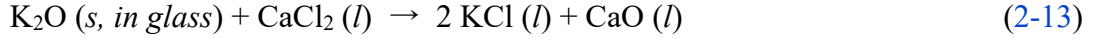
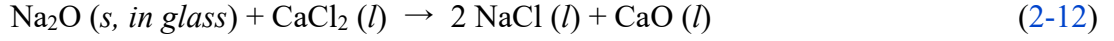
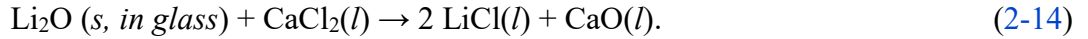


Figure 2-7 Potential- pO^{2-} diagrams for (a) the Na–Ca–O–Cl system and (b) the K–Ca–O–Cl system in molten $CaCl_2$ at 1123 K. (red dashed line: boundary between Si and other compounds in Si–Ca–O–Cl system).



2.3.5 Li and Zn–Ca–O–Cl system

Figure 2-8(a) shows the potential– $p\text{O}^{2-}$ diagram for the Li–Ca–O–Cl system in molten CaCl_2 at 1123 K. The red dashed lines in the diagram show the boundaries of SiCl_4/Si , SiO_2/Si and calcium silicates/Si reported under the same conditions. The upper sides of the dashed lines are the stable regions of SiCl_4 , SiO_2 and calcium silicates. The lower sides are the stable region of Si. The stable phase is $\text{LiCl}(l)$, which readily dissolves in molten CaCl_2 . Because the electrochemical window of molten $\text{LiCl}(l)$ is 3.35 V, the deposition of $\text{Li}(l)$ occurs at -0.08 V (vs. Ca^{2+}/Ca) when the activity change of $\text{LiCl}(l)$ in molten $\text{CaCl}_2(l)$ is not considered. Therefore, as with the Na–Ca–O–Cl system (in Section 2.3.4), the chemical reaction between the $\text{Li}_2\text{O} (s, \text{ in glass})$ and molten $\text{CaCl}_2(l)$ proceeds as follows:



The potential– $p\text{O}^{2-}$ diagram for the Zn–Ca–O–Cl system is shown in Figure 2-8(b). The $p\text{O}^{2-}$ value at the boundary between ZnO and $\text{ZnCl}_2(g)$ is 4.32. The potential between ZnO and Zn is 1.84 V vs. Ca^{2+}/Ca at $p\text{O}^{2-} = 4.32$. In the range of $p\text{O}^{2-} > 4.32$, Zn species are thought to evaporate from the system in the form of $\text{ZnCl}_2(g)$ at a more positive potential than 1.84 V. At $p\text{O}^{2-} < 4.32$, the boundary for $\text{ZnO}/\text{elemental Zn}$ located at more positive potential than those for $\text{SiO}_2/\text{elemental Si}$ and calcium silicates/elemental Si. At negative potentials, where both of Zn and Si are in the elemental phase, Si will dissolve in liquid Zn at up to 6 mol% [28]. In addition, liquid Zn might evaporate because the experimental temperature of 1103 K is close to its boiling point (1180 K). However, when the molten salt covers liquid Zn layer, the evaporation of Zn is suppressed [29].

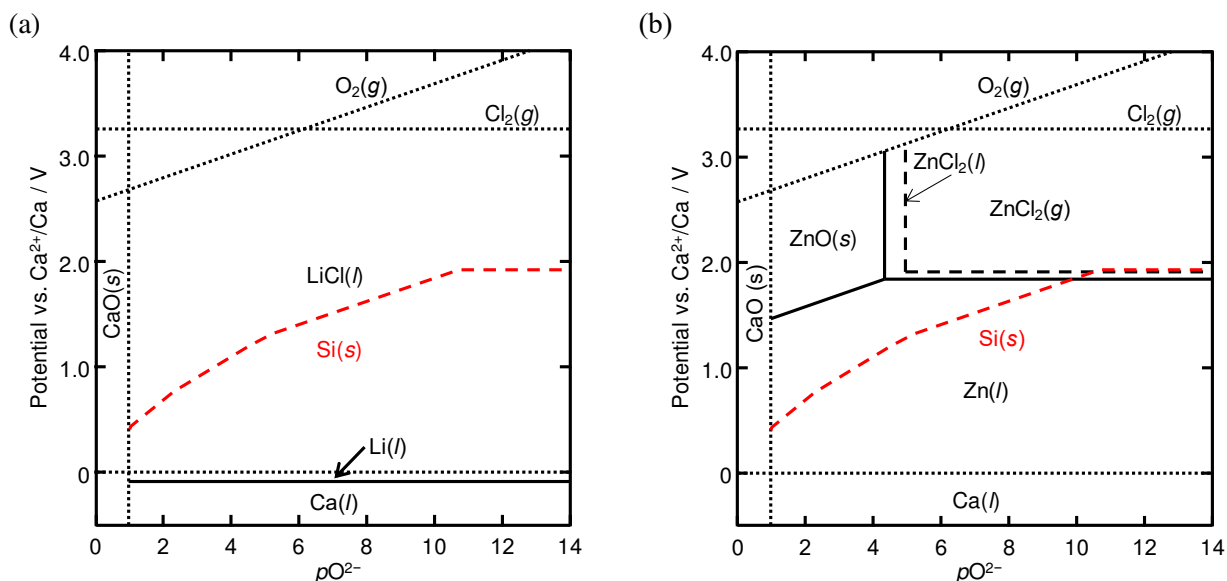


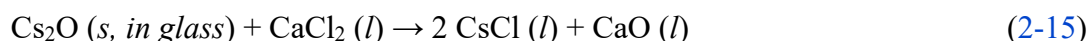
Figure 2-8 Potential- pO^{2-} diagrams for the (a) Li-Ca-O-Cl system and (b) Zn-Ca-O-Cl system in molten $CaCl_2$ at 1123 K. Red dashed line shows the boundary between Si and other compounds in the Si-Ca-O-Cl system.

2.3.6 Zr, Cs, Pd, and Se-Ca-O-Cl system (LLFP oxides)

Figure 2-9(a) shows the potential- pO^{2-} diagram for the Zr-Ca-O-Cl system. At $pO^{2-} = 2.59$, $CaZrO_3$ equilibrates with ZrO_2 . Unlike the Zn-Ca-O-Cl system, the ZrO_2/Zr and $CaZrO_3/Zr$ boundaries are more negative than those for SiO_2/Si and calcium silicates/Si, which are indicated by the red dashed lines. The potential for the three-phase boundary of $ZrO_2/CaZrO_3/Zr$, 0.56 V, is more negative than that for $SiO_2/CaSiO_3/Si$, 1.32 V, in the Si-Ca-O-Cl system. This reveals that it is more difficult to reduce ZrO_2 to elemental Zr compared to SiO_2 . As for chlorides, only $ZrCl_4(g)$ appears in the diagram. According to a review paper by Abdelkader *et al.* [30], other phases such as ZrO_{2-x} [31][32] and Ca_xZrO_β [33] have been reported. If the thermodynamic data for these compounds were available, the potential- pO^{2-} diagram for the Zr-Ca-O-Cl would change, especially the boundary between Zr and ZrO_2 . Moreover, because several alloys exist in the Si-Zr system [34], these alloys would form in the region surrounded by the boundary lines between Si/ SiO_2 (or silicates) (red-dotted line) and Zr/ ZrO_2 . Liu *et al.* [35] reported the formation of Si-Zr intermetallic compounds such as SiZr and Si_2Zr by the electrochemical reduction of $ZrSiO_4$ and

ZrSiO₄–SiO₂ mixed powders in molten CaCl₂–NaCl at 1073 K.

The potential– pO^{2-} diagram for the Cs–Ca–O–Cl system is shown in Figure 2-9(b). The only stable phase is pure chloride, CsCl(*l*), which is similar to the Li–Ca–O–Cl. Thus, the dissolution of Cs₂O in the melt is thermodynamically favorable.



The formation potential of Cs(*g*) calculated from the thermodynamic data of CsCl(*l*) is –0.14 V vs. Ca²⁺/Ca.

The potential– pO^{2-} diagram for the Pd–Ca–O–Cl systems is shown in Figure 2-9(c). The stable phases are Pd(*s*) and PdCl₂(*l*). The potential of the boundary between Pd and PdCl₂ is 3.20 V. Because several alloys exist in the Pd–Si system [36], some alloys can be formed at negative potentials.

Figure 2-9(d) shows the potential– pO^{2-} diagram for the Se–Ca–O–Cl system. There are stable regions for Se₂(*g*), SeO₂(*g*), and SeCl₂(*g*) at more positive than 1.72 V. At the more negative potential, CaSe(*s*) is stable. The boundary among Se₂(*g*), SeO₂(*g*), and SeCl₂(*g*) is located at 3.01 V and $pO^{2-} = 6.42$. From the diagram, selenium compounds are expected to be evaporated out of the system at the potential more positive than 1.72 V. If CaSe(*s*) is formed by electrolysis, Se stays in the solid phase. However, the behavior of the Se is difficult to be predicted because some Se compounds may dissolve into molten CaCl₂. Since Li₂Se was reported to be soluble in LiCl–KCl [37], CaSe(*s*) would have a certain solubility in CaCl₂.

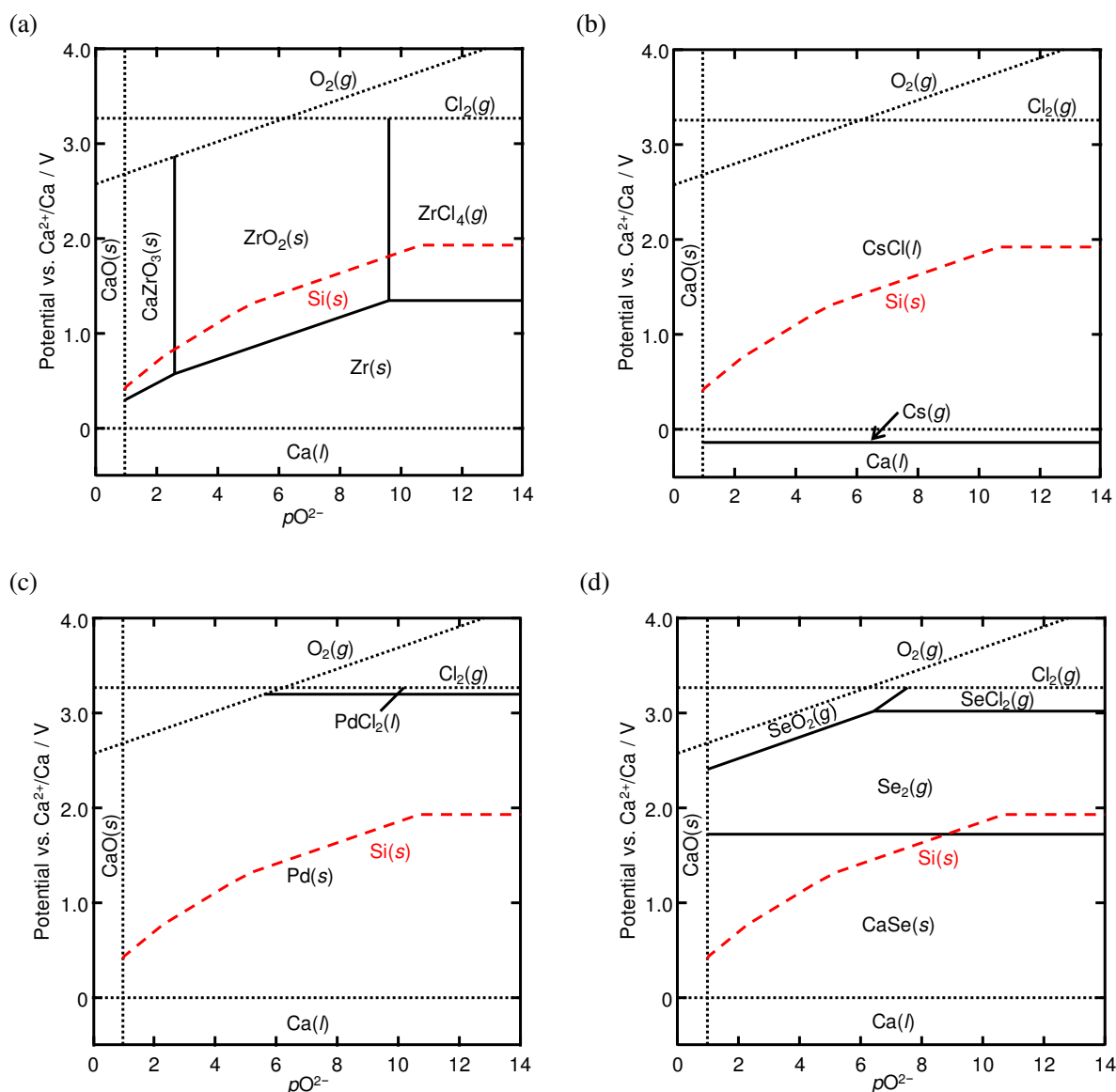


Figure 2-9 Potential- pO^{2-} diagrams for the (a) Zr-Ca-O-Cl system, (b) Cs-Ca-O-Cl system, (c) Pd-Ca-O-Cl system, and (d) Se-Ca-O-Cl system in molten $CaCl_2$ at 1123 K. Red dashed line shows the boundary between Si and other compounds in the Si-Ca-O-Cl system.

2.3.7 Summary for the predicted behaviors of elements in simulant 2

Table 2-1 summarizes the predicted behaviors of elements in simulant 2 after immersion or electrolysis at 0.6 V in molten $CaCl_2$ at 1123 K. Here, the potential of immersion is assumed to be 2.2 V (rest potential). In this table, the behaviors are predicted from the states (solid, liquid, and gas) of stable compounds at 2.2 V and 0.6 V Ca^{2+}/Ca in potential- pO^{2-} diagrams. The behaviors of some selected elements are described below. Li and Cs are dissolved into molten $CaCl_2$. Zr remains

in the solid phase in the region of $pO^{2-} < 9.60$. Pd exists in a metallic state at the more negative potential than 3.20 V. Zn evaporates as $ZnCl_2(g)$ at the more positive potential than 1.84 V. In the more negative potential region, Zn is stable as elemental $Zn(l)$. $CaSe(s)$ is formed by electrolysis at the more negative potential than 1.72 V. At the more positive potential, $Se_2(g)$ is stable.

Table 2-1 Summary for the predicted behaviors of elements in simulant 2 after immersion or electrolysis at 0.6 V in molten $CaCl_2$ at 1123 K.

Element	Immersion (Rest potential: 2.2 V vs. Ca^{2+}/Ca)		Electrolysis (0.6 V vs. Ca^{2+}/Ca)	
	Compound	Behavior	Compound	Behavior
Si	$Ca_3SiO_5 (s)$ $Ca_3Si_2O_7 (s)$ $CaSiO_3 (s)$ $SiO_2 (s)$	Remaining (Partially dissolution)	$Ca_3SiO_5 (s)$ $Si (s)$	Remaining
B	$Ca_3B_2O_6 (s)$ $Ca_2B_2O_5 (s)$ $CaB_2O_4 (s)$ $CaB_4O_7 (s)$ $B_2O_3 (l)$	Remaining (Partially dissolution)	$Ca_3B_2O_6 (s)$ $B (s)$	Remaining
Na	$NaCl (l)$	Dissolution	$NaCl (l)$	Dissolution
Al	$CaAl_{12}O_{19}(s)$ $Ca_3Al_2O_6 (s)$ $Ca_{12}Al_{14}O_{33} (s)$ $CaAl_2O_4 (s)$ $CaAl_4O_7 (s)$ $Al_2O_3 (s)$	Remaining	$CaAl_{12}O_{19}(s)$ $Ca_3Al_2O_6 (s)$ $Ca_{12}Al_{14}O_{33} (s)$ $CaAl_2O_4 (s)$ $CaAl_4O_7 (s)$ $Al (l)$	Remaining
Li	$LiCl (l)$	Dissolution	$LiCl (l)$	Dissolution
Zn	$ZnO (s)$ $ZnCl_2 (g)$	Remaining or Evaporation	$Zn (l)$	Remaining
Pd	$Pd (s)$	Remaining	$Pd (s)$	Remaining
Zr	$CaZrO_3 (s)$ $ZrO_2 (s)$	Remaining	$CaZrO_3 (s)$ $ZrO_2 (s)$ $Zr (s)$	Remaining
Cs	$CsCl (l)$	Dissolution	$CsCl (l)$	Dissolution
Se	$Se_2 (g)$	Evaporation	$CaSe (s)$	Remaining

2.3.8 Other systems

2.3.7.1 Uranium

Figure 2-10 shows the potential– pO^{2-} diagram for the U–Ca–O–Cl system in molten $CaCl_2$ at 1123 K. Although uranium is not contained in simulant 3, the prediction of the electrochemical reduction behavior of UO_2 in molten $CaCl_2$ is very important because the real vitrified waste contains uranium. The calcium uranate appears in the low pO^{2-} region, and the uranium oxychlorides such as $UOCl(s)$, $UOCl_2(s)$, and $UO_2Cl_2(l)$ appear in small regions in the diagrams. The stable regions for $U_3O_8(s)$, $U_4O_9(s)$, and $UO_2(s)$ locate at the positive potential. The chlorides, $UCl_4(g)$, and $UCl_3(l)$ are stable in the high pO^{2-} region.

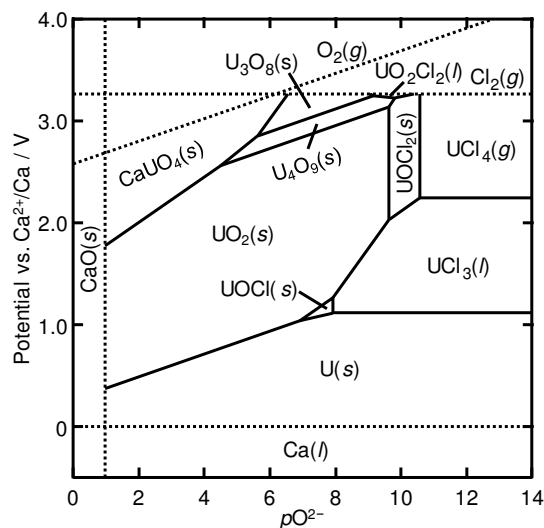
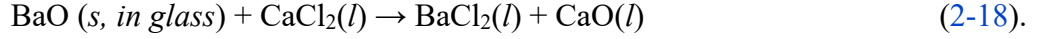
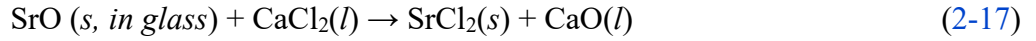
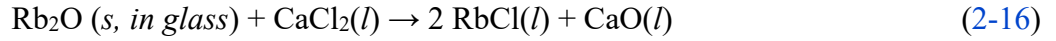


Figure 2-10 Potential– pO^{2-} diagrams for the U–Ca–O–Cl system in molten $CaCl_2$ at 1123 K.

2.3.7.2 Alkali and alkali earth elements ($M = Rb, Sr, \text{ and } Ba$)

Figure 2-11(a)(b)(c) the potential– pO^{2-} diagrams for the (a) Rb, (b) Sr, and (c) Ba–Ca–O–Cl systems. The stable phases are only chlorides which should readily dissolve into molten $CaCl_2$. Here, the stable phase of $SrCl_2$ is described as solid since melting point of $SrCl_2$ (1147 K) is above 1123 K. As mentioned in Section 2.2, dissolution of constituent oxides proceeds only when they are immersed in molten $CaCl_2$:



Since the electrochemical windows of $\text{RbCl}(l)$, $\text{SrCl}_2(s)$, and $\text{BaCl}_2(l)$ are larger than CaCl_2 , metal deposition of Rb, Sr, and Ba does not occur even at the negative potential of Ca^{2+}/Ca .

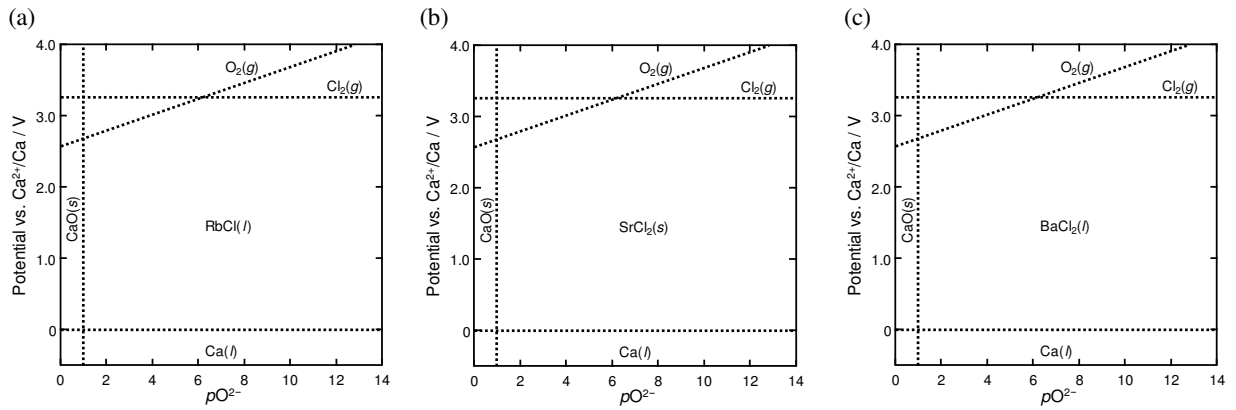


Figure 2-11 Potential- $p\text{O}^{2-}$ diagrams for (a) Rb-Ca-O-Cl, (b) Sr-Ca-O-Cl, and (c) Ba-Ca-O-Cl system in molten CaCl_2 at 1123 K.

2.3.7.3 Rare earth elements ($M = \text{Y, La, Ce, Pr, Nd, Sm, Eu, and Gd}$)

Figure 2-12(a)–(h) show the potential- $p\text{O}^{2-}$ diagrams for the (a) Y–, (b) La–, (c) Ce–, (d) Pr–, (e) Nd–, (f) Sm–, (g) Eu–, and (h) Gd–Ca–O–Cl systems. In all the diagrams, chlorides are stable in the high $p\text{O}^{2-}$ region. The diagrams for the Y–, La–, Ce–, Pr–, Nd–, and Gd–Ca–O–Cl systems have the stable region of the metals at negative potential. On the other hand, there are no stable region of metallic Sm and Eu for the Sm– and Eu–Ca–O–Cl systems due to the high stability of chlorides. The systems of La–, Nd–, Sm–, Eu–, and Gd–Ca–O–Cl have the stable region of oxychlorides. For the Ce– and Pr–Ca–O–Cl systems, several types of oxides are stable in the corresponding diagrams.

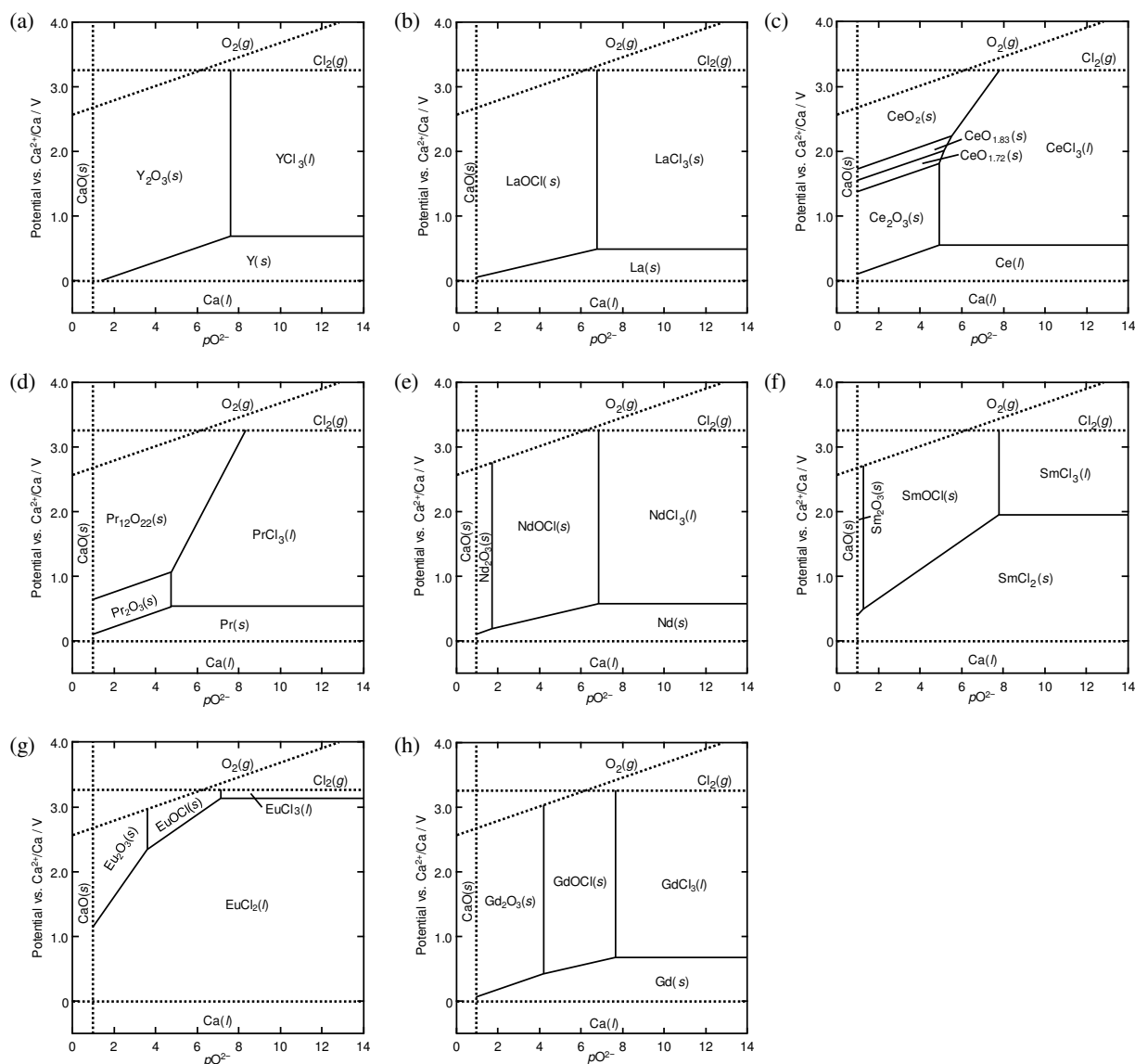


Figure 2-12 Potential- pO^{2-} diagrams for (a) Y-Ca-O-Cl, (b) La-Ca-O-Cl, (c) Ce-Ca-O-Cl, (d) Pr-Ca-O-Cl, (e) Nd-Ca-O-Cl, (f) Sm-Ca-O-Cl, (g) Eu-Ca-O-Cl, and (h) Gd-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

2.3.7.4 Precious metal group elements ($M = Ru, Rh, \text{ and } Ag$)

Figure 2-13(a)(b)(c) show the potential- pO^{2-} diagrams for the (a) Ru-, (b) Rh-, and (c) Ag-Ca-O-Cl systems. Metallic Ru and Rh have the large stable region. In the diagram for the Ru-Ca-O-Cl system, $RuO_2(s)$ appears at the positive potential and near the oxygen gas evolution region. In the diagram for the Rh-Ca-O-Cl system, two oxides and two chlorides appear at the positive potential region. In the Ag-Ca-O-Cl system, the stable compounds are $AgCl(l)$ and

Ag(s). The equilibrium potential between AgCl(l) and Ag(s) is 2.45 V. As indicated in the plot of Figure 2-2, Ag is more stable than Ag₂O due to the positive Gibbs energy of formation of Ag₂O.

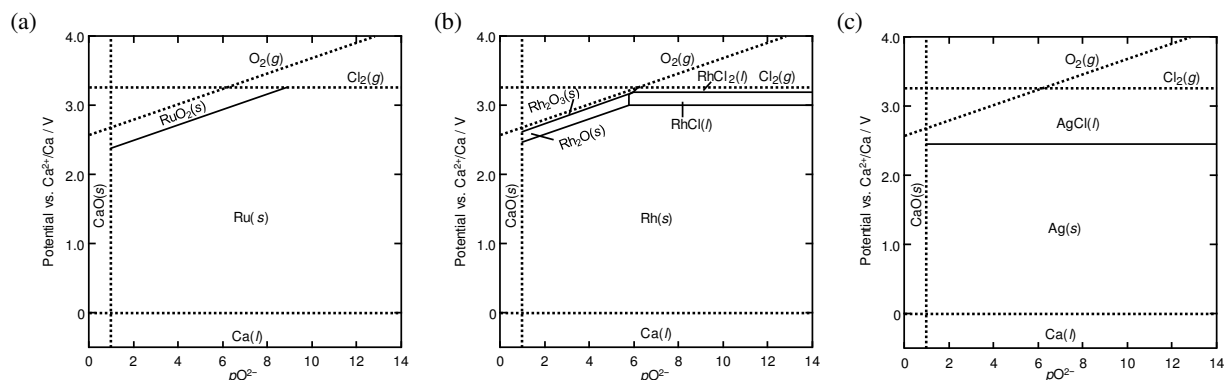


Figure 2-13 Potential- pO^{2-} diagrams for (a) Ru-Ca-O-Cl, (b) Rh-Ca-O-Cl, and (c) Ag-Ca-O-Cl system in molten CaCl₂ at 1123 K.

2.3.7.5 Groups 14 to 16 ($M = P, Sn, \text{ and } Te$)

Figure 2-14(a)–(c) shows the potential- pO^{2-} diagrams for the (a) P–, (b) Sn–, and (c) Te–Ca–O–Cl systems. For all three diagrams, Ca–M compounds and elemental states appear in the negative potential region. In the diagram for the P–Ca–O–Cl system, two types of Ca–P–O compounds are stable at the positive potential. Elemental P is stable as gas phase at this temperature. Oxychloride gas and two types of chloride gases are stable at the high pO^{2-} and positive potential region. In the diagram for the Sn–Ca–O–Cl system, the metallic Sn region exists in the middle potential range. SnO₂(s) and SnCl₂O₂(g) are stable at the positive potential and low pO^{2-} region. Two types of chlorides are stable in the high pO^{2-} and positive potential region. In the diagram for the Te–Ca–O–Cl system, CaTe(s) and elemental Te(l) are stable at more negative potential than 2.07 V. TeO(l) and TeCl₂(g) appear at the positive potential.

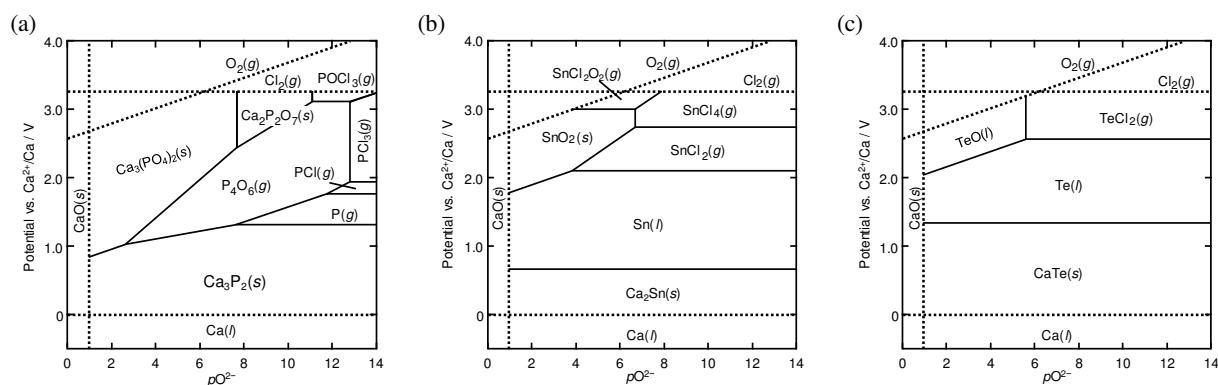


Figure 2-14 Potential- pO^{2-} diagrams for (a) P-Ca-O-Cl, (b) Sn-Ca-O-Cl, and (c) Te-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

2.3.7.6 Other transition elements ($M = Cr, Mn, Fe, Ni, \text{ and } Mo$)

Figure 2-15(a)–(e) show the potential- pO^{2-} diagrams for the (a) Cr–, (b) Mn–, (c) Fe–, (d) Ni–, and (e) Mo–Ca–O–Cl systems. For all the systems, stable regions of metals are located in the potential more negative than 1 V. In the Cr–Ca–O–Cl system, three types of chlorides exist in the high pO^{2-} and positive potential region. Calcium chromate is stable in the low pO^{2-} and positive potential region. In the Mn–Ca–O–Cl system, a large stable region for $MnCl_2(l)$ appears in the high pO^{2-} and positive potential region. Also, three types of oxides are stable at the low pO^{2-} and positive potential. In the diagram of Fe–Ca–O–Cl system, two types of chlorides are stable in the high pO^{2-} and positive potential region. Then, three types of oxides appear near the chloride region. At the lowest pO^{2-} region, the stable region of calcium iron oxide exists. In the Ni–Ca–O–Cl system, there exist three stable regions of $NiO(s)$, $NiCl_2(g)$ and $Ni(s)$. Three-phase equilibrium point locates at $E = 2.65$ V and $pO^{2-} = 7.10$. In the Mo–Ca–O–Cl system, two types of calcium molybdates are stable with a relatively large region with low pO^{2-} and positive potential values. There are several stable regions for the compounds such as $MoO_2(s)$, $MoCl_2O_2(g)$, and $MoCl_3O(g)$. Two types of chlorides are stable at more positive potential than 2.54 V.

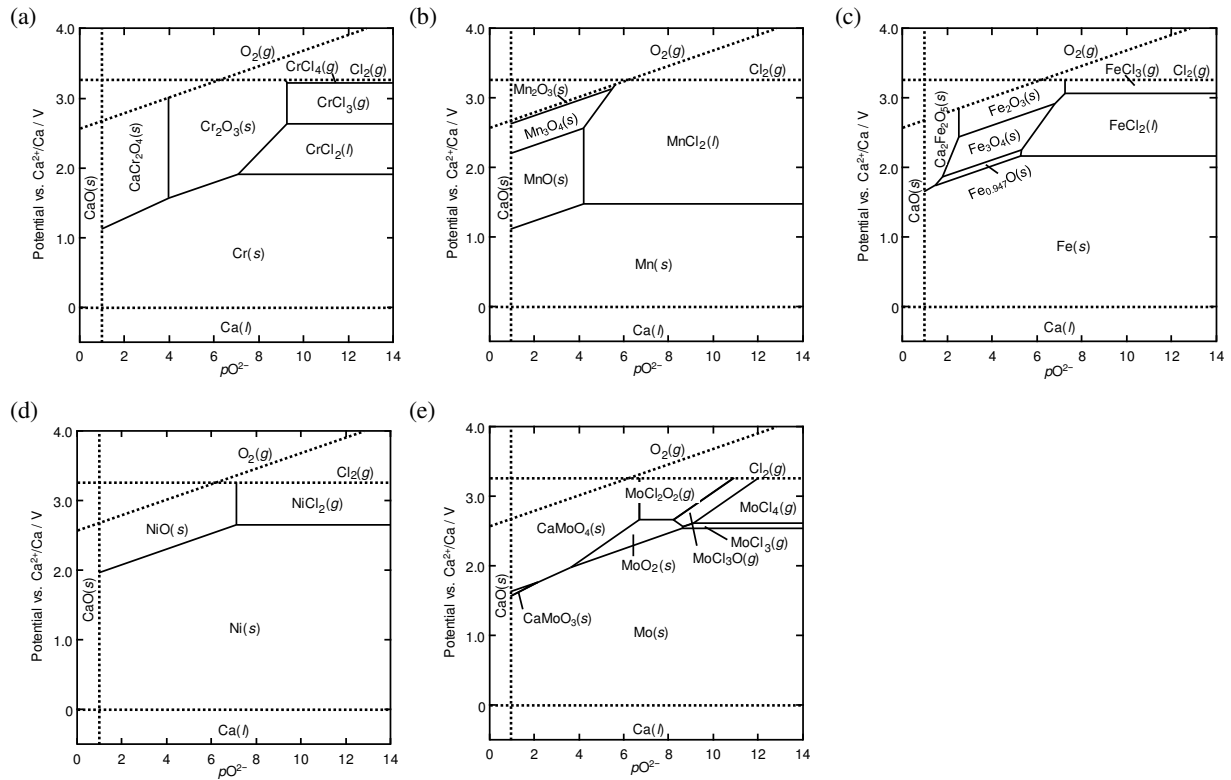


Figure 2-15 Potential- pO^{2-} diagrams for (a) Cr-Ca-O-Cl, (b) Mn-Ca-O-Cl, (c) Fe-Ca-O-Cl, (d) Ni-Ca-O-Cl, and (e) Mo-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

2.4 Conclusion

Based on the thermodynamic calculations, the reduction behavior of 33 oxides contained in simulant 3 is predicted. Alkali and alkali-earth elements such as Na and Ba are dissolved into molten $CaCl_2$. Most of precious metals and transition metals such as B, Zn, Pd, Ru, Sn, Cr, and Ag are stable as a metallic state at the potential where SiO_2 is reduced to Si. Al, Zr, REE, Se, and Te are stable in the solid as other chemical state when SiO_2 is reduced to Si. REE are possibly dissolved into $CaCl_2$. Zn, Se, Sn, P, and Te are possibly evaporated from the system. The electrochemical reduction behaviors of constituent oxides are predicted using potential- pO^{2-} diagrams constructed from thermodynamic data.

2.5 Thermodynamic data

Table 2-2 shows the thermodynamic data used for the calculations.

Table 2-2 Thermodynamic data used for the calculations.

System	Compound	Phase	Standard Gibbs energy of formation / kJ mol^{-1}	References
Ca–O–Cl (Frame)	CaCl_2^*	Liquid	–629.56	[38]
	CaO^*	Solid	–517.42	[38]
	CaO	Liquid	–496.40	[17]
Si–Ca–O–Cl	SiO_2^*	Solid	–708.94	[39]
	SiCl_4^*	Gas	–515.20	[38,40]
	CaSi_2	Solid	–97.09	[21]
	Ca_3Si_4	Solid	–277.17	[21]
	CaSi	Solid	–88.63	[21]
	Ca_5Si_3	Solid	–358.41	[21]
	Ca_2Si	Solid	–130.33	[21]
	CaSiO_3	Solid	–1317.21	[41–43]
	Ca_3SiO_5	Solid	–2432.12	[44]
	$\text{Ca}_3\text{Si}_2\text{O}_7$	Solid	–3227.78	[44]
B–Ca–O–Cl	B_2O_3^*	Liquid	–992.35	[38][41,42]
	BCl_3^*	Gas	–346.18	[38]
	CaB_6	Solid	–89.03	[45]
	CaB_2O_4	Solid	–1623.02	[38][43,46]
	CaB_4O_7	Solid	–2619.79	[38][43,46]
	$\text{Ca}_2\text{B}_2\text{O}_5$	Solid	–2224.55	[41,42]
	$\text{Ca}_3\text{B}_2\text{O}_6$	Solid	–2798.66	[41,42]
Al–Ca–O–Cl	Al_2O_3^*	Solid	–1320.18	[47,48]
	AlCl_3^*	Gas	–525.56	[38]
	Al_2Ca	Solid	–65.08	[23]
	$\text{CaAl}_{12}\text{O}_{19}$	Solid	–8510.7	[38,41–43]
	CaAl_2O_4	Solid	–1879.12	[39,46,49]
	CaAl_4O_7	Solid	–3211.68	[38,41–43]
	$\text{Ca}_3\text{Al}_2\text{O}_6$	Solid	–2925.99	[41–43]
	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	Solid	–15790.18	[39]
Na–Ca–O–Cl	Na_2O^*	Solid	–261.37	[39]
	Na_2O_2	Liquid	–277.54	[38,50]
	NaCl^*	Liquid	–309.32	[38,41,42,51]
K–Ca–O–Cl	K_2O^*	Liquid	–197.23	[38,40]
	K_2O_2	Liquid	–237.68	[38,40]
	KCl^*	Liquid	–326.16	[41,42]

Li–Ca–O–Cl	Li ₂ O*	Solid	–448.14	[38,40–42]
	LiCl*	Liquid	–322.75	[38,41,42,50]
Zn–Ca–O–Cl	ZnO*	Solid	–234.38	[38,41,42,52]
	ZnCl ₂ *	Gas	–274.15	[38,41,42,52]
Zr–Ca–O–Cl	ZrO ₂ *	Solid	–886.91	[38,40–42]
	CaZrO ₃	Solid	–1439.49	[38,39,53]
	ZrCl ₂	Liquid	–273.00	[38,40,54]
	ZrCl ₃	Gas	–486.57	[38,40]
	ZrCl ₄ *	Gas	–739.54	[38–40]
Cs–Ca–O–Cl	Cs ₂ O*	Liquid	–181.62	[38,40]
	CsCl*	Liquid	–327.78	[38,40]
Pd–Ca–O–Cl	PdO*	Solid	3.57	[39,46,49]
	PdCl ₂ *	Liquid	–12.12	[39]
Se–Ca–O–Cl	SeO ₂ *	Gas	–211.91	[38,40]
	SeCl	Liquid	–333.08	[47,48,55]
	SeCl ₄ *	Solid	22.63	[38,47,48,56]
	CaSe	Solid	–437.13	[47,48]
U–Ca–O–Cl	UCl ₃	Liquid	–621.89	[46]
	UCl ₄	Gas	–720.71	[38,40,57]
	UO ₂	Solid	–890.51	[38,58]
	U ₄ O ₉	Solid	–3662.49	[38,56]
	U ₃ O ₈	Solid	–2831.34	[38,56]
	UO ₂ Cl ₂	Liquid	–902.39	[38,46]
	UOCl	Solid	–659.73	[41,42,57]
	UOCl ₂	Solid	–815.79	[39,57]
Rb–Ca–O–Cl	CaUO ₄	Solid	–1584.37	[39]
	Rb ₂ O*	Liquid	–176.82	[38,40]
Sr–Ca–O–Cl	RbCl*	Liquid	–320.89	[38,40]
	SrCl ₂ *	Solid	–662.25	[54]
Ba–Ca–O–Cl	SrO*	Solid	–479.83	[38,40]
	BaCl ₂ *	Solid	–680.30	[41–43]
Y–Ca–O–Cl	BaO*	Solid	–444.36	[38,41,42]
	YCl ₃ *	Liquid	–743.79	[41,42]
La–Ca–O–Cl	Y ₂ O ₃ *	Solid	–1579.14	[59]
	LaCl ₃ *	Solid	–802.60	[38,41,42]
Ce–Ca–O–Cl	La ₂ O ₃ *	Solid	–1475.87	[38,41,42,60]
	LaOCl	Solid	–815.67	[39,46,49]
	CeCl ₃ *	Liquid	–786.38	[38,41,42,53]
Pr–Ca–O–Cl	CeO _{1.72}	Solid	–801.78	[47,48]
	CeO _{1.83}	Solid	–825.87	[47,48]
	CeO ₂	Solid	–857.22	[38–40]
	Ce ₂ O ₃ *	Solid	–1492.39	[38,41,42,61]
	PrCl ₃ *	Liquid	–790.78	[41,42]
Nd–Ca–O–Cl	Pr ₇ O ₁₂	Solid	–5412.67	[38,56]
	Pr ₂ O ₃ *	Solid	–1489.75	[38–40]
	Pr ₁₂ O ₂₂	Solid	–10517.46	[46]
	NdCl ₃ *	Liquid	–779.04	[46]
Nd–Ca–O–Cl	Nd ₂ O ₃ *	Solid	–1491.94	[38,40,46]
	NdOCl	Solid	–793.85	[41,42]

Sm–Ca–O–Cl	SmCl ₂	Solid	–639.29	[39]
	SmCl ₃ *	Liquid	–765.52	[38,56]
	Sm ₂ O ₃ *	Solid	–1495.95	[38,41,42,51]
	SmOCl	Solid	–800.76	[46]
Eu–Ca–O–Cl	EuCl ₂	Liquid	–650.51	[55]
	EuCl ₃ *	Liquid	–663.72	[38,56]
	EuO	Solid	–479.36	[38,40,46]
	Eu ₂ O ₃ *	Solid	–1312.66	[46]
	EuOCl	Solid	–684.13	[55]
Gd–Ca–O–Cl	GdCl ₃ *	Liquid	–748.38	[38,56]
	Gd ₂ O ₃ *	Solid	–1517.92	[38,40,47,48]
	GdOCl	Solid	–780.28	[38,40–42]
Ru–Ca–O–Cl	RuCl ₄ *	Gas	52.34	[39]
	RuO ₂ *	Solid	–118.64	[39]
Rh–Ca–O–Cl	RhCl	Liquid	–25.99	[55]
	RhCl ₂	Liquid	–33.80	[55]
	RhCl ₃ *	Liquid	–19.67	[39,46,49]
	Rh ₂ O	Solid	–43.64	[47,48]
	Rh ₂ O ₃ *	Solid	–68.56	[47,48,62]
Sn–Ca–O–Cl	SnCl ₂	Gas	–224.18	[38,40,46]
	SnCl ₄ *	Gas	–325.36	[38,40,46]
	SnCl ₂ O ₂	Gas	–398.85	[38,53]
	Ca ₂ Sn	Solid	–258.37	[47,48]
	SnO ₂ *	Solid	–348.64	[41,42,49,59]
P–Ca–O–Cl	PCl	Gas	–144.10	[38,49,54]
	PCl ₃ *	Gas	–398.82	[38,40–42]
	P ₄ O ₆ *	Gas	–2450.01	[38,40,46]
	POCl ₃	Gas	–570.53	[38,50]
	Ca ₃ P ₂	Solid	–758.98	[47,48,63]
	Ca ₂ P ₂ O ₇	Solid	–2930.48	[43,46]
	Ca ₃ (PO ₄) ₂	Solid	–3592.75	[41,42]
Te–Ca–O–Cl	CaTe	Solid	–257.94	[41,42]
	TeCl ₂ *	Liquid	–134.63	[39,46,49]
	TeO*	Liquid	–122.27	[55]
Cr–Ca–O–Cl	CrCl ₂	Liquid	–260.95	[38,40]
	CrCl ₃ *	Gas	–321.11	[38,40]
	CrCl ₄	Gas	–324.81	[38,40]
	CaCr ₂ O ₄	Solid	–1423.00	[46]
	Cr ₂ O ₃ *	Solid	–840.52	[54]
Mn–Ca–O–Cl	MnCl ₂ *	Liquid	–344.14	[46]
	MnO*	Solid	–302.22	[38,41,42]
	Mn ₂ O ₃	Solid	–669.22	[41,42,47–49]
	Mn ₃ O ₄	Solid	–998.16	[41,42]
Fe–Ca–O–Cl	FeCl ₂	Liquid	–210.78	[38,52]
	FeCl ₃ *	Gas	–229.95	[38,40,46]
	Fe _{0.947} O	Liquid	–191.52	[38,49,54,56]
	Fe ₃ O ₄	Solid	–753.04	[39]
	Fe ₂ O ₃ *	Solid	–528.76	[38,52]
	Ca ₂ Fe ₂ O ₅	Solid	–1631.53	[46]

Ni–Ca–O–Cl	NiCl ₂ *	Gas	–117.82	[38,52]
	NiO*	Solid	–137.90	[38,58]
Mo–Ca–O–Cl	MoCl ₃	Gas	–169.71	[38,40,46]
	MoCl ₄ *	Gas	–272.47	[38,50]
	MoCl ₂ O ₂	Gas	–501.01	[54]
	MoCl ₃ O	Gas	–398.72	[38,40]
	MoO ₂ *	Solid	–385.12	[38,49,54]
	CaMoO ₃	Solid	–949.76	[64]
	CaMoO ₄	Solid	–1153.01	[39,46,49]
Ag–Ca–O–Cl	AgCl*	Liquid	–78.24	[38,46,49]
	Ag ₂ O*	Liquid	38.20	[38]
	AgO	Gas	–119.07	[38,55]

Asterisk (*) marks : the values used in the plot in [Figure 2-2](#).

2.6 Reference list

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Chapter 3

Electrochemical reduction of borosilicate glass

3.1 Introduction

In this chapter, the electrochemical reduction of borosilicate glass in molten CaCl_2 was investigated with the aim of developing a new pretreatment method for the vitrified radioactive wastes. Since the reduction behavior of the actual vitrified radioactive wastes is expected to be complicated, borosilicate glass was selected as the study object. Specifically, Pyrex[®] glass was chosen from among the many kinds of borosilicate glass because it was the most typical one. The electrochemical behavior of Pyrex[®] glass was studied by cyclic voltammetry and the results were compared to those of SiO_2 . Here, glass-seal electrodes [1–4], which give good reproducibility for the geometry of the glass/conductor/ CaCl_2 three-phase zone, were employed. Potentiostatic electrolysis was conducted at several selected potentials to prepare the samples for instrumental analysis. Based on these results, the electrochemical reduction behavior of borosilicate glass was determined.

3.2 Experimental

Figure 3-1 shows a schematic of the experimental apparatus. 500 g of CaCl_2 (> 95.0 %, Wako Pure Chemical Industries, Ltd.) crushed in a mortar was placed in an alumina crucible (outer diameter: 90 mm, height: 140 mm, purity 99%, As One Corp.) and put in an open dry chamber (HRW-60AR, Daikin Co. Ltd.). Then, the CaCl_2 was dried at 453 K in a vacuumed oven for more than 72 h, transferred to a quartz glass vessel, and vacuumed at 773 K for 24 h to further remove

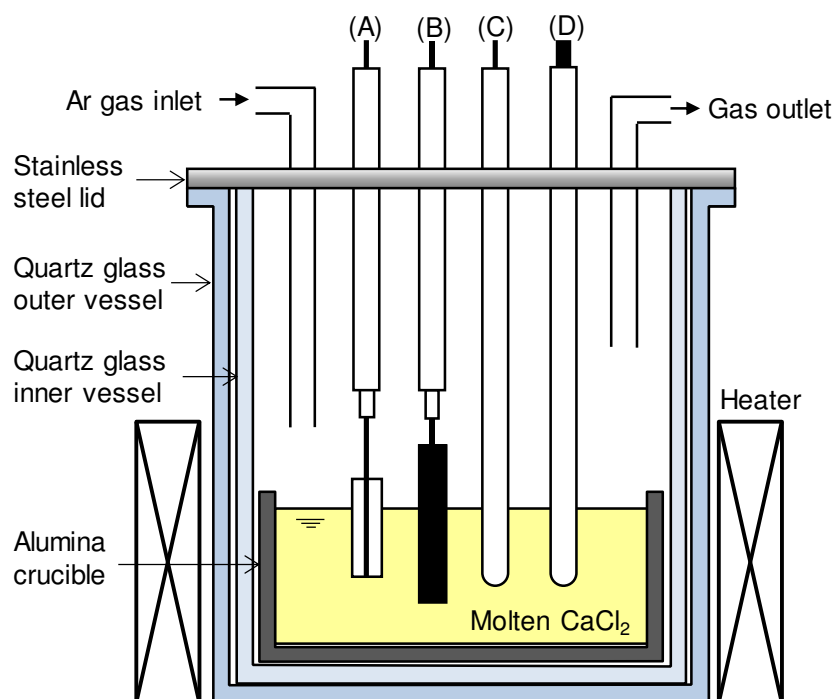
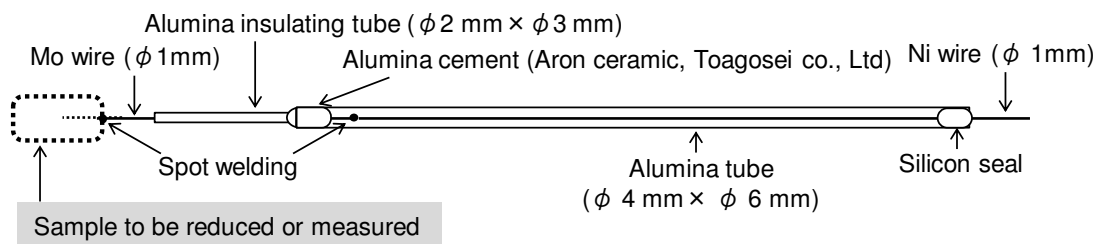


Figure 3-1 Schematic of the experimental apparatus. (A) Working electrode, (B) graphite counter electrode, (C) Ag^+/Ag reference electrode, and (D) thermocouple.

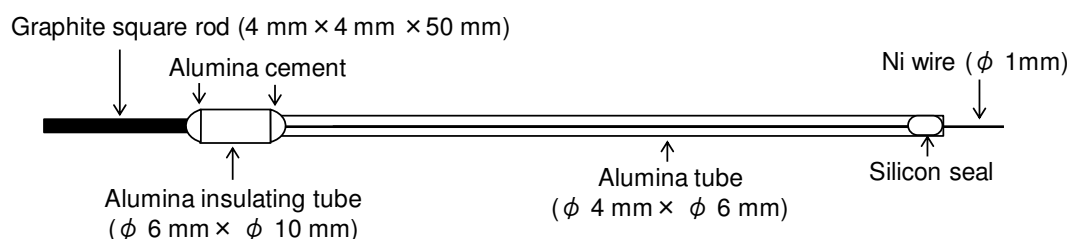
moisture. The subsequent electrochemical experiments were conducted inside the quartz glass vessel at 1123 K under a dry Ar atmosphere (Kyoto Teisan Co. Ltd., purity > 99.999%).

Electrochemical measurements and potentiostatic electrolysis were conducted with a three-electrode method using an electrochemical measurement system (HZ-3000, Hokuto Denko Corp.). Figure 3-2 shows schematics of the experimental apparatus. (a) Working electrode, and (b) graphite counter electrode, (c) Ag^+/Ag reference electrode. The working electrode was Mo electrode. When the potential of Ca deposition was confirmed, no additional object was attached. In the other case, the sample or electrode, described in the was spot welded. The counter electrode was a graphite square rod (4 mm × 4 mm × 50 mm) and the reference electrode was an Ag^+/Ag electrode [5]. The potential was calibrated by the Ca deposition/dissolution potential measured by Mo electrode [5]. Glass-seal electrodes (Figure 3-3(a)) and wire-wound electrodes (Figure 3-3(b)) were used as the working electrodes. In the glass-seal electrodes, a tungsten rod (> 99.95%,

(a) Working electrode (Mo)



(b) Counter electrode (graphite)



(c) Reference electrode (Ag^+/Ag)

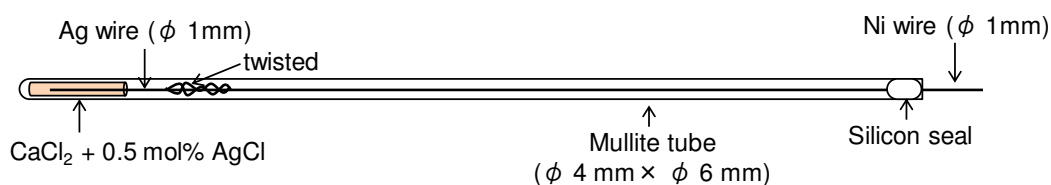


Figure 3-2 Schematic of the experimental apparatus. (A) Working electrode, (B) graphite counter electrode, (C) Ag^+/Ag reference electrode, and (D) thermocouple.

diameter: 2.0 mm, Nilaco corp.) was sealed in a borosilicate glass tube (Pyrex[®], SiO_2 80.8 wt%, B_2O_3 12.5 wt%, Al_2O_3 2.3 wt%, Na_2O 4.0 wt%, K_2O 0.4 wt%, o.d. 8 mm) or a silica (SiO_2) glass tube (o.d. 6 mm). In the wire-wound electrodes, a borosilicate glass plate (Tempex[®], SiO_2 81 wt%, B_2O_3 13 wt%, Al_2O_3 2 wt%, Na_2O 3.3 wt%, K_2O 0.7 wt%, 5 mm × 15 mm × 1.1 mm) or a silica glass plate (5 mm × 15 mm × 1 mm) was wound by a Mo wire (diam. 0.2 mm, > 99.95%, Nilaco Corp.) [6]. A chromel-alumel thermocouple inserted in an alumina tube was used for the temperature control.

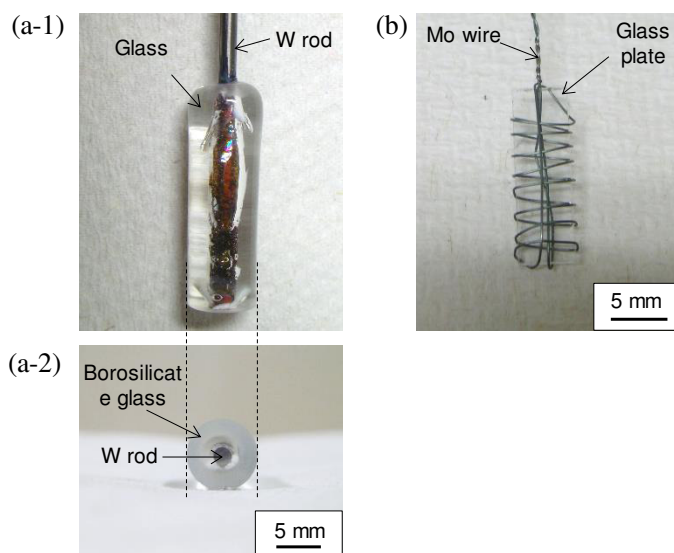


Figure 3-3 Photographs of (a-1) the side view and (a-2) the cross-sectional view of a glass-seal electrode and (b) a wire-wound electrode.

Following potentiostatic electrolysis, the glass-sealed electrodes were rinsed with distilled water to remove residual salts, dried at room temperature, and cut by a diamond cutter into ~5 mm long sections. The prepared samples were evaluated using an optical digital microscope (Dino Lite PRO Polarizer DILITE30 AM-413ZT, Sanko Co., Ltd.) and a scanning electron microscope (SEM; VE-8800, Keyence Corp.). They were also characterized by energy dispersive X-ray spectroscopy (EDX; EDAX Genesis APEX2, AMETEK Co. Ltd.), X-ray diffractometry (XRD; Ultima IV, Cu-K α line, Rigaku Corp.), X-ray photoelectron spectroscopy (XPS, JPS-9010MC, JEOL Ltd.), and Raman spectroscopy (Nano finder 30, wavelength: 532 nm, Tokyo Instruments Inc.). For the cross-sectional mapping of elements, a sample obtained in the reduction of glass-sealed electrode was cut and embedded in acrylic resin and polished. Then, SEM/Wavelength dispersive X-ray (WDX) spectroscopy (JXA-8530F, JEOL Ltd.) at an accelerating voltage of 10 kV was used. For the XPS and Raman spectrum measurement, potentiostatic electrolysis was conducted at 0.9 V vs. Ca²⁺/Ca for 60 minutes, and the samples were rinsed with distilled water, 8 % HCl aqueous solution, and 10 % NaOH aqueous solution, successively. For XPS measurement, the powdery products recovered from the reduced glass-sealed electrodes were fixed evenly on carbon tape and then etched by Ar ion irradiation to remove the natural oxide from

the surface. The spectra were calibrated by the C *1s* peak at 284.8 eV for the reduced sample and by the Si–O peak at 103.3 eV for the unreduced sample. When the wire-wound electrodes after electrolysis was analyzed by XRD, the Mo wire was cut and removed from the plate carefully. In the case of observation by SEM, the Mo wire was not removed from the plate.

3.3 Results and discussion

3.3.1 The chemical reaction between the glass and molten CaCl_2

Figure 3-4(a-1) shows a photograph of the borosilicate glass plate after immersion in molten CaCl_2 for 30 min. A deformation of the glass plate is observed because Mo wire was wound in one fixed direction around the plate and the glass has a low softening point at around 1093 K. Furthermore, the devitrification of the plate, namely the color change from transparent to white, is observed. The devitrification suggests the occurrence of reactions between the glass surface and the melt. A surface SEM image and the EDX result are shown in Figure 3-4(a-2) and (a-3), respectively. The composition of the original plate is calculated from the composition ratio of each oxide in the borosilicate glass. The flake-like deposits of 1–5 μm in size in the dimples (point 1) are richer in Ca and Al compared with the original glass plate. Conversely, the porous surface (point 2) has areas with compositions similar to that of the original state, without the decrease of Na. The decrease of Na concentration is confirmed for both points 1 and 2. These behaviors suggest that the reaction of Na_2O with CaCl_2 results in the devitrification of the glass.

To confirm the progress of the chemical reaction into the inner bulk of the glass, a fractured section of the broken plate (Figure 3-4(b-1)) was observed by SEM/EDX (Figure 3-4(b-2) and (b-3)). At point 3, the small holes in the porous phase have sizes of less than 1 μm . This porous phase has a similar composition to that of the original state, except for the decrease of Na. The porous phase has a similar morphology and composition to that of the porous phase observed by surface SEM at point 2. At point 4, the depth of the dimples near the flake-like deposits is around 10 μm , which agrees with the surface observation at point 2 in Figure 3-4(a-2). The flake-

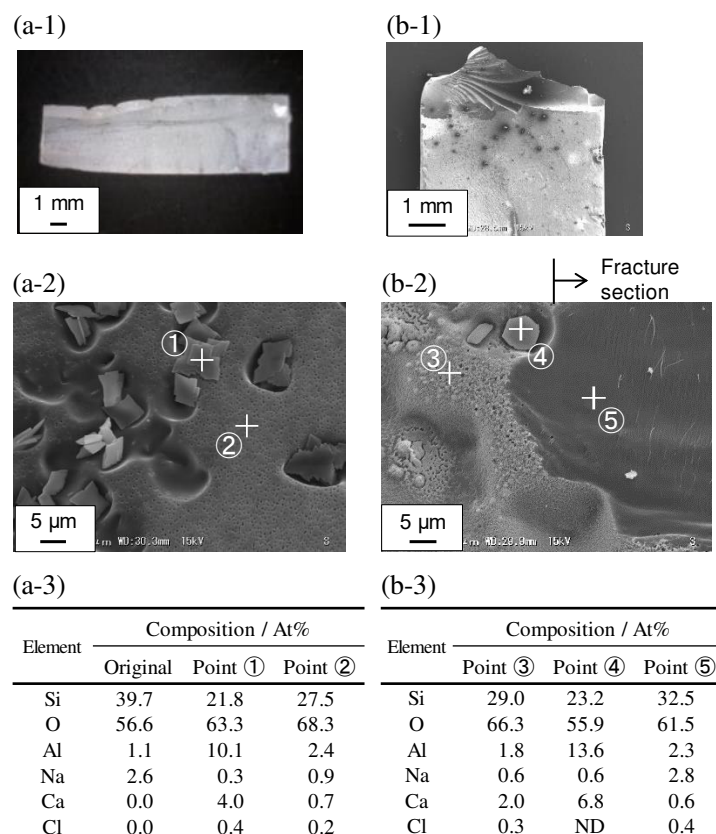


Figure 3-4 (a-1) A microscope image, (a-2) SEM image, and (a-3) EDX analysis result for a borosilicate glass plate soaked in molten CaCl_2 for 30 min at 1123 K and rinsed by distilled water. SEM images in (b-1) low and (b-2) high magnification and (b-3) EDX analysis result from a fractured surface obtained by breaking the plate after immersion shown in (a-1).

like deposits (point 4) have a higher concentration of Ca and Al than that of the original glass, and a similar composition to that of the flake-like deposits at the surface (at point 1). At point 5, the fractured section has a smooth morphology at the micrometer scale. The composition is similar to that of the original state, and the concentration of Na is the same as that for the original composition. Therefore, it is concluded that the phase separation occurs only on the surface of the glass. The dissolution of Na_2O into the melt (Equation 2-1) is also suggested by the potential- $p\text{O}^{2-}$ diagram in Figure 2-7(a). Although the behavior of K was not clarified due to the small K content, its oxide should also dissolve in the melt (Equation 2-2) according to Figure 2-7(b).

Considering the technique for the chemical strengthening of glass by ion exchange in molten salts [7], the present results are reasonable. In the ion exchange process at temperature

above the strain point, smaller ions are introduced to replace larger ones. For example, a soda-lime-silica glass soaked in a lithium-containing bath is strengthened by the exchange of Li^+ with Na^+ (ion radius: $\text{Na}^+ > \text{Li}^+$) [8]. In the present study, the strain points for Pyrex and Tempax glass (783 and 791 K, respectively) are lower than 1123 K, and therefore the Ca^{2+} ions replace Na^+ ions (ion radius: $\text{Na}^+ > \text{Ca}^{2+}$).

For phase separation, the mechanism is explained as follows: The dissolution of Na_2O into the molten CaCl_2 results in an increase of the concentration of O^{2-} ions around the glass surface. According to the report, the higher content of CaO promotes the phase separation of $\text{SiO}_2\text{--CaO--Al}_2\text{O}_3$ glass into a $(\text{CaO--Al}_2\text{O}_3)$ -rich phase and a SiO_2 -rich phase at 1173 K [9]. Thus, Ca and Al rich flake-like deposits and porous phase are observed only on the glass surface after immersion in molten CaCl_2 .

3.3.2 Cyclic voltammetry

Figure 3-5(a) and (b) show the cyclic voltammograms for sealed borosilicate glass and silica glass electrodes in molten CaCl_2 at 1123 K, respectively. The voltammograms were recorded for five consecutive cycles. The apparent current density is expressed with respect to the bottom area (the exposed area) of the tungsten rod. In the voltammogram for borosilicate glass (Figure 3-5(a)), a small cathodic current was observed at 1.8 V vs. Ca^{2+}/Ca , which is more positive than the reduction potential of SiO_2 at 1.3 V (Figure 3-5(b)). Moreover, both the cathodic currents during the negative scan and the anodic currents during the positive scan at around 1.3 V are clearly larger than those for the silica glass. These results are explained by the reduction of some oxides that are less stable than SiO_2 . From the potential- $p\text{O}^{2-}$ diagrams for Si--Ca--O--Cl and B--Ca--O--Cl (Figure 2-3 and 2-4), the reduction of B_2O_3 is suggested to occur at more positive potentials than that of SiO_2 in the whole range of $p\text{O}^{2-}$ values. Thus, the cathodic current at 1.8 V is attributed to the reduction of B_2O_3 .

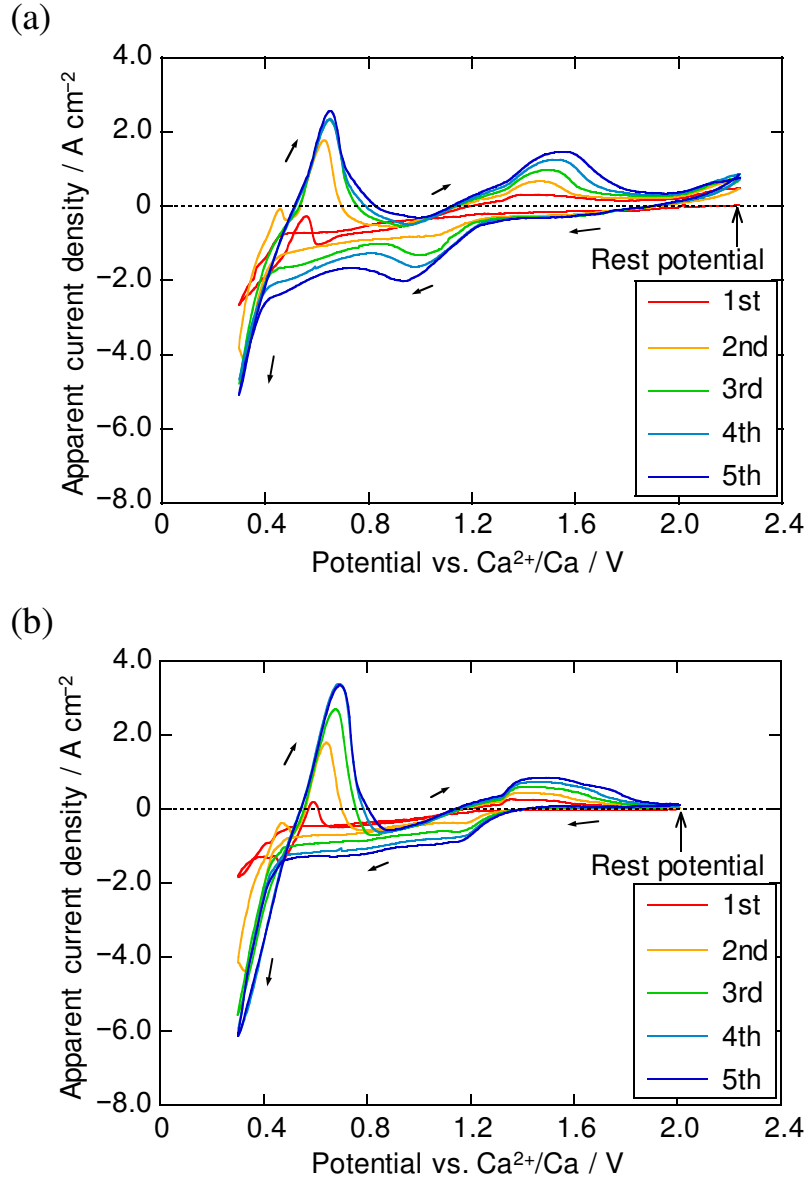
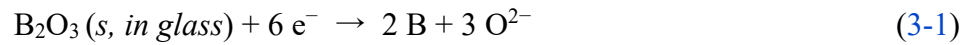
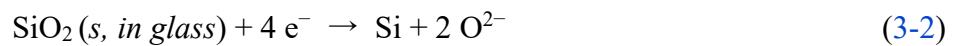


Figure 3-5 Cyclic voltammograms for sealed (a) borosilicate and (b) silica glass electrodes in molten CaCl_2 at 1123 K. Scan rate: 100 mV s^{-1} .



A large cathodic current flows from 1.3 V, which corresponds to the reduction of SiO_2 to Si. The large current is due to the large composition ratio of SiO_2 in the glass.



A sharp increase of cathodic current is observed at 0.4 V, which can be explained by the formation of Si–Ca alloys [6,10].



After the switching potential at 0.3 V, an anodic current peak is observed at 0.65 V for dissolution of Ca from the Si–Ca alloy. Another anodic current peak at 1.5 V correspond to the oxidation of Si to SiO₂. A small anodic current observed from 1.8 V is likely due to the oxidation of B to B₂O₃.

In both cases, the currents increase as the cycles are repeated. For pure SiO₂, this behavior has been explained by the increase of the reaction zone due to the formation of conductive Si from insulating SiO₂ [11]. A similar mechanism is possible for the reduction of borosilicate glass.

3.3.3 Potentiostatic electrolysis (glass-sealed electrode)

To confirm the reduction reaction results, potentiostatic electrolysis was conducted using borosilicate glass-sealed electrodes at 0.6 V (B-1), 0.9 V (B-2), and 1.4 V (B-3), and silica glass-sealed electrodes at 0.6 V (S-1), 0.9 V (S-2), and 1.4 V (S-3) for 30 minutes in molten CaCl₂ at 1123 K. Figure 3-6 shows current-time curves during the potentiostatic electrolysis and Figure 3-7 shows the microscope images of the reduced glass-sealed electrodes. In the electrolysis at 0.9 V and 0.6 V, the reduction currents for borosilicate glass are larger than those for silica glass. On the other hand, in Figure 3-7(a), the reduced area looks smaller for borosilicate glass compared to that of silica glass. This outcome is confirmed by Figure 3-7(b), where the surface reduction progressed to the side of the tube in the case of silica glass at 0.6 V. These results indicate the smaller surface reaction rate for borosilicate glass. The observed larger current and slower surface reaction for borosilicate glass are explained by its faster inner direction progress As shown in the cross-sectional image for sample B-2 (Figure 3-7(c)), the depth of the reduced portion for borosilicate glass is almost the same length as the reduced portion on the surface. At 1.4 V, the observed current is larger

for borosilicate glass compared to that of silica glass, which is consistent with the cyclic voltammetry results. However, the current value is much smaller compared to the electrolysis at more negative potentials. Since noticeable change is not observed in the microscope images, the reduction did not proceed in bulk for either borosilicate glass or silica glass.

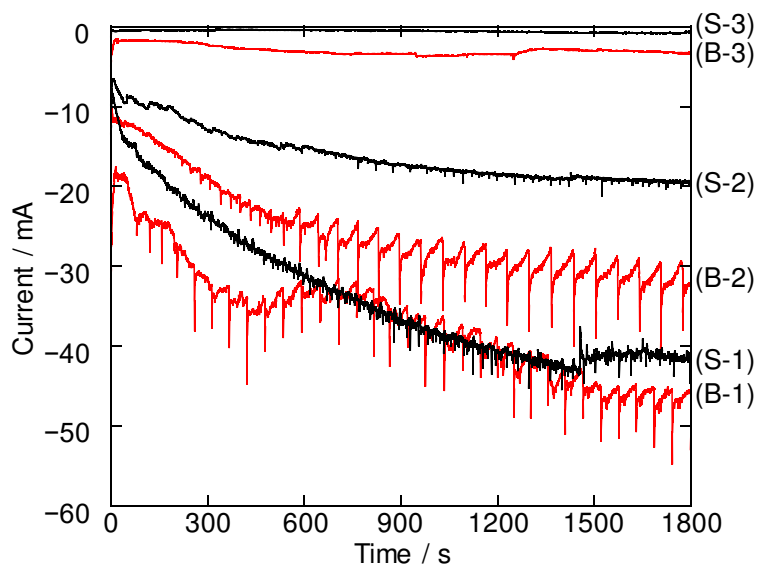


Figure 3-6 Current-time curves during the potentiostatic electrolysis of the sealed borosilicate glass electrodes at (B-1) 0.6 V, (B-2) 0.9 V, and (B-3) 1.4 V and the sealed silica glass electrodes at (S-1) 0.6 V and (S-2) 0.9 V vs. Ca^{2+}/Ca for 30 minutes in molten CaCl_2 at 1123 K.

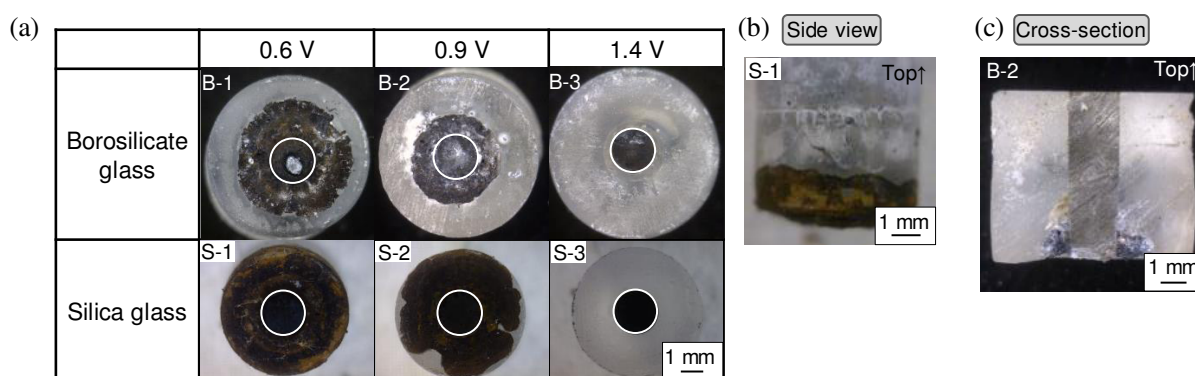
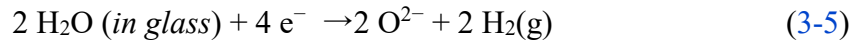
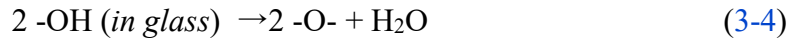


Figure 3-7 (a) Microscope images of the sealed glass electrodes following potentiostatic electrolysis at 0.6 V, 0.9 V, and 1.4 V vs. Ca^{2+}/Ca for 30 minutes in molten CaCl_2 at 1123 K. White circle shows the boundary between the tungsten rod and the glass. (b) A surface side view of sample S-1. (c) A cross-sectional view of sample B-2.

3.3.4 Potentiostatic electrolysis (wire-wound electrode)

The wire-wound borosilicate glass electrodes were potentiostatically electrolyzed to investigate its reduction behavior at different potentials (0.6, 0.9, and 1.4 V). A larger current is observed at more negative potential (Figure 3-8(a)). As seen in Figure 3-8(b), the plate color changes from colorless to brown at 0.6 and 0.9 V, while no change is observed for 1.4 V. The area of color change is larger at 0.6 V than at 0.9 V. At 1.4 V, bubbles are formed in the glass at the contact points with the Mo wire. Bubbles are also observed in the borosilicate glass at 0.9 and 0.6 V.

The bubbles in the glass are thought to be formed by H₂ gas generated from water reduction in the glass. There is a report that silanols ($\equiv\text{Si-OH}$) remain both on the surface and inside the silica (SiO₂) at 1123 K, and H₂O is generated by the reaction in Equation 3-4 when the temperature increases [12].



If these reactions occur, H₂ gas is generated near the contact point between the Mo wire and the surface of the glass. These bubbles are not observed for the silica glass plate at 1.4, 0.9, and 0.6 V [6]. The difference in the behaviors of borosilicate glass and silica glass is also likely due to the softening points (SiO₂: 1773 K, Tempax glass: 1093 K). In the case of borosilicate glass, H₂ gas can deform the glass because of the low softening point, allowing bubbles to form at the contact points with the Mo wire.

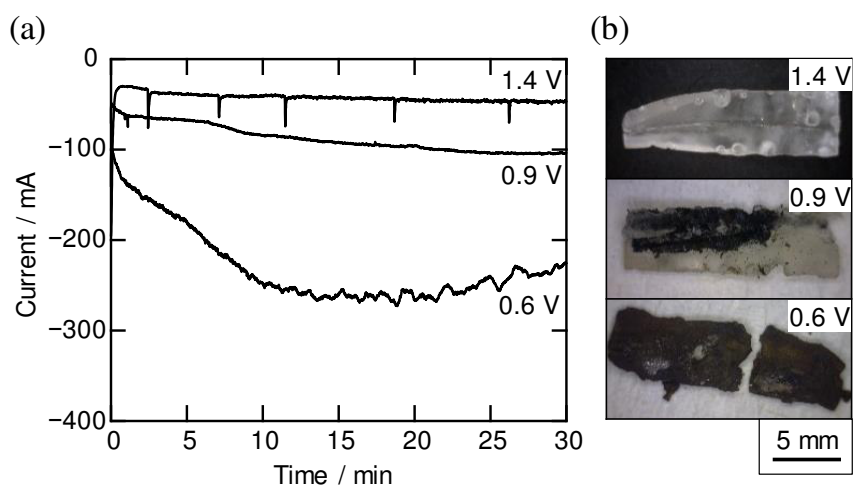


Figure 3-8 (a) Current-time curves during the reduction of wire-wound borosilicate glass electrodes at 0.6, 0.9, and 1.4 V vs. Ca^{2+}/Ca for 30 min in CaCl_2 at 1123 K and (b) microscope images of the obtained samples prepared by the electrolysis.

3.3.5 Characterization of the products

Figure 3-9 shows the XRD patterns for the reduced (a) borosilicate glass plate and (b) silica glass plate at 0.9 V in molten CaCl_2 at 1123 K. The formation of crystalline silicon was confirmed for both samples.

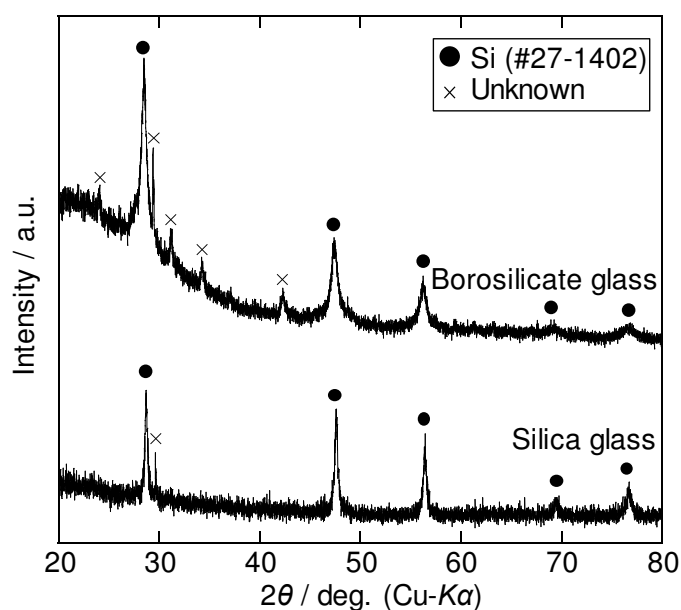


Figure 3-9 XRD patterns for the reduced (a) borosilicate glass plate and (b) silica glass plate following electrolytic reduction at 0.9 V vs. Ca^{2+}/Ca for 30 minutes in molten CaCl_2 at 1123 K.

The results of the SEM observation and EDX analysis of the reduction products of borosilicate glass at 0.6 and 0.9 V (Figure 3-10) indicate the reduction of SiO_2 to Si. The formation of connected granular products with a high concentration of Si is observed at both potentials. The size of the grains is smaller at 0.6 than that at 0.9 V. The largest diameter of the grains is *ca.* 1 μm at 0.6 V and *ca.* 10 μm at 0.9 V. At 0.6 V (Figure 3-10(a)), the connected granular products grow from regions of high Si and low O concentrations (point 1) toward regions of high O concentration (point 2).

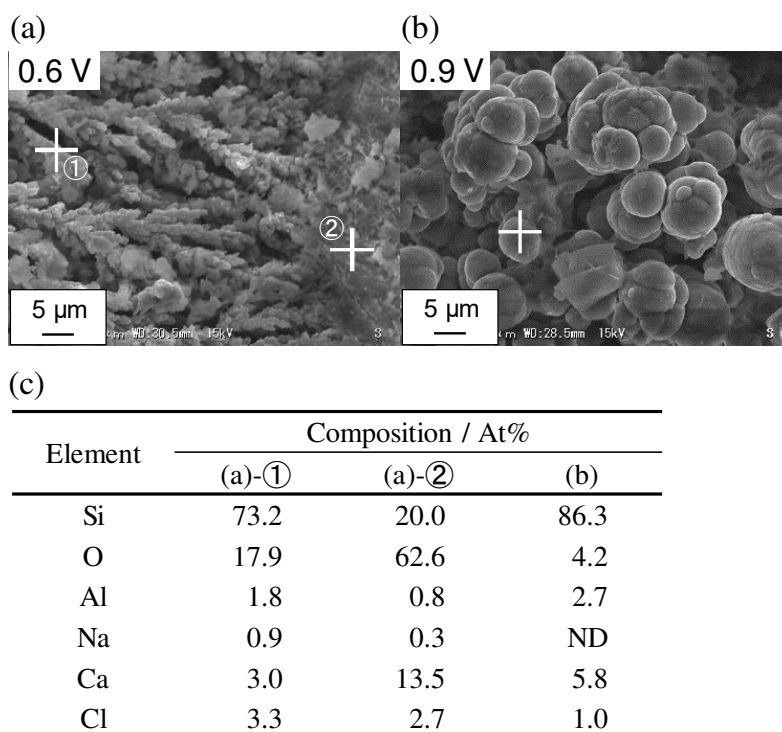


Figure 3-10 SEM images of reduction products obtained by the electrochemical reduction of a borosilicate glass plate at (a) 0.6 and (b) 0.9 V vs. Ca^{2+}/Ca for 30 min. (c) EDX analysis results for each sample.

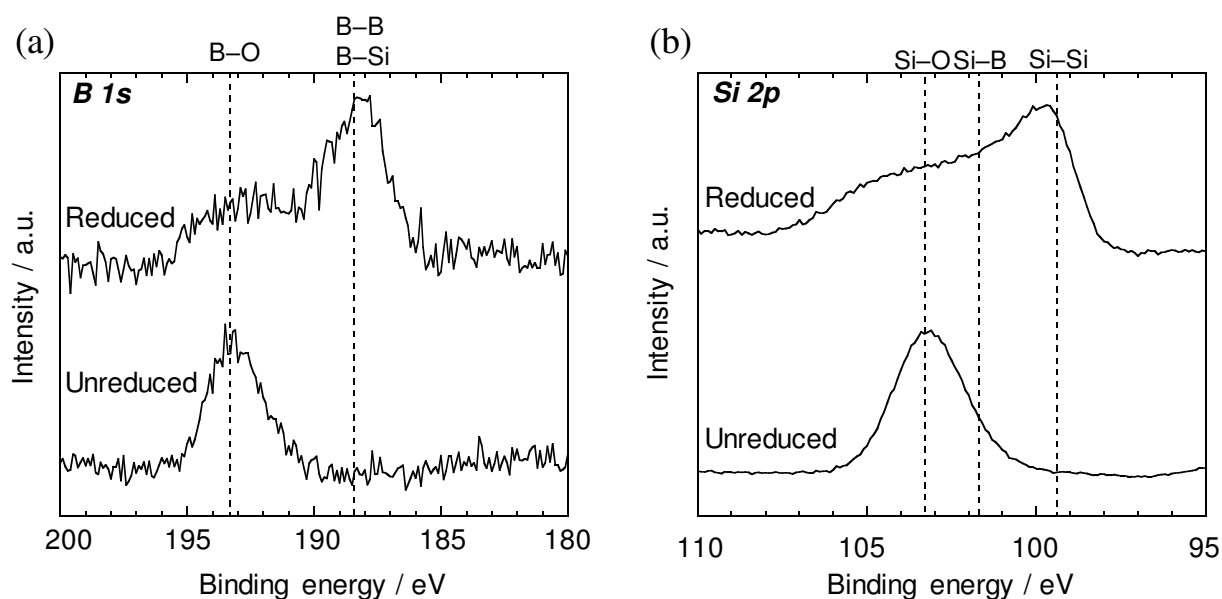


Figure 3-11 XPS spectra for (a) B *1s* and (b) Si *2p* for the borosilicate glass samples before and after the electrolytic reduction at 0.9 V vs. Ca^{2+}/Ca for 60 minutes in CaCl_2 at 1123 K.

The dissolution of Na_2O into molten CaCl_2 during the electrochemical reduction was confirmed by SEM/EDX analysis for both 0.6 and 0.9 V. The concentrations of Na for all three points in Figure 3-10 are lower than the initial Na concentration of the plate (2.6 wt%). These results agree with the reaction between borosilicate glass and molten CaCl_2 in the immersion experiment, as discussed in Section 3.3.6.

Figure 3-11 shows XPS spectra for (a) B *1s* and (b) Si *2p* before and after the reduction of borosilicate samples. In Figure 3-11(a), a weakened B–O peak and a strengthened B–B or B–Si peak are observed for the reduced sample, which confirm the reduction of boron oxide to its metallic state. In the same manner, the reduction of silicon oxide to its metallic state is confirmed in Figure 3-11(b), agreeing with the XRD analysis.

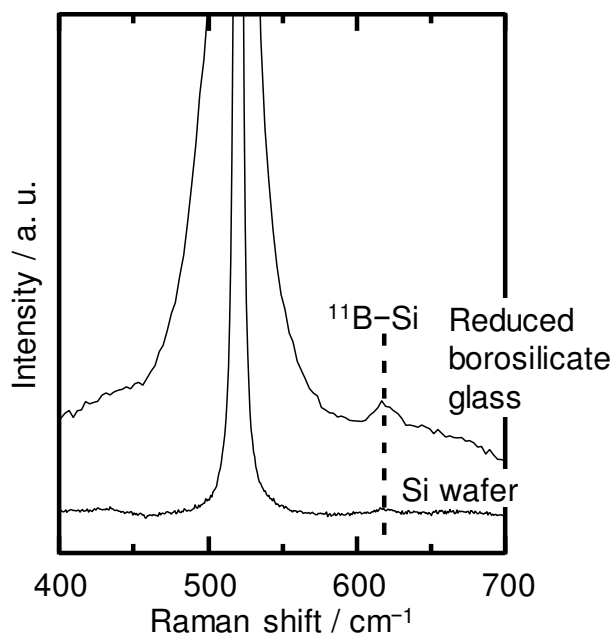


Figure 3-12 Raman spectra for the borosilicate glass reduced at 0.9 V vs. Ca^{2+}/Ca for 30 min in CaCl_2 and p-type single crystal silicon wafer. A 532 nm-excitation laser was used

To investigate the reduction behavior of B, Raman spectroscopy was conducted for the borosilicate glass reduced at 0.9 V for 30 min in CaCl_2 , as shown in [Figure 3-12](#). For reference, the spectrum of a p-type single crystal silicon wafer was also measured. In addition to the peak for crystalline Si (520 cm^{-1}), a small peak at 618 cm^{-1} appears for the reduced borosilicate glass. The peak position agrees well with the reported values for $^{11}\text{B-Si}$ (620 cm^{-1}) in B-doped bulk silicon [\[13\]](#) and $^{11}\text{B-Si}$ (618 cm^{-1}) in B-doped Si-nanowire [\[14\]](#). In this study, the author used natural boron (^{11}B : 80.2%, ^{10}B : 19.8%) and the more abundant $^{11}\text{B-Si}$ peak was detected. Therefore the reduction of B_2O_3 in the borosilicate glass, which was suggested by the cyclic voltammetry and potential- $p\text{O}^{2-}$ diagram, is confirmed. The reduced products have B-Si bonds in a B-containing crystalline Si phase.

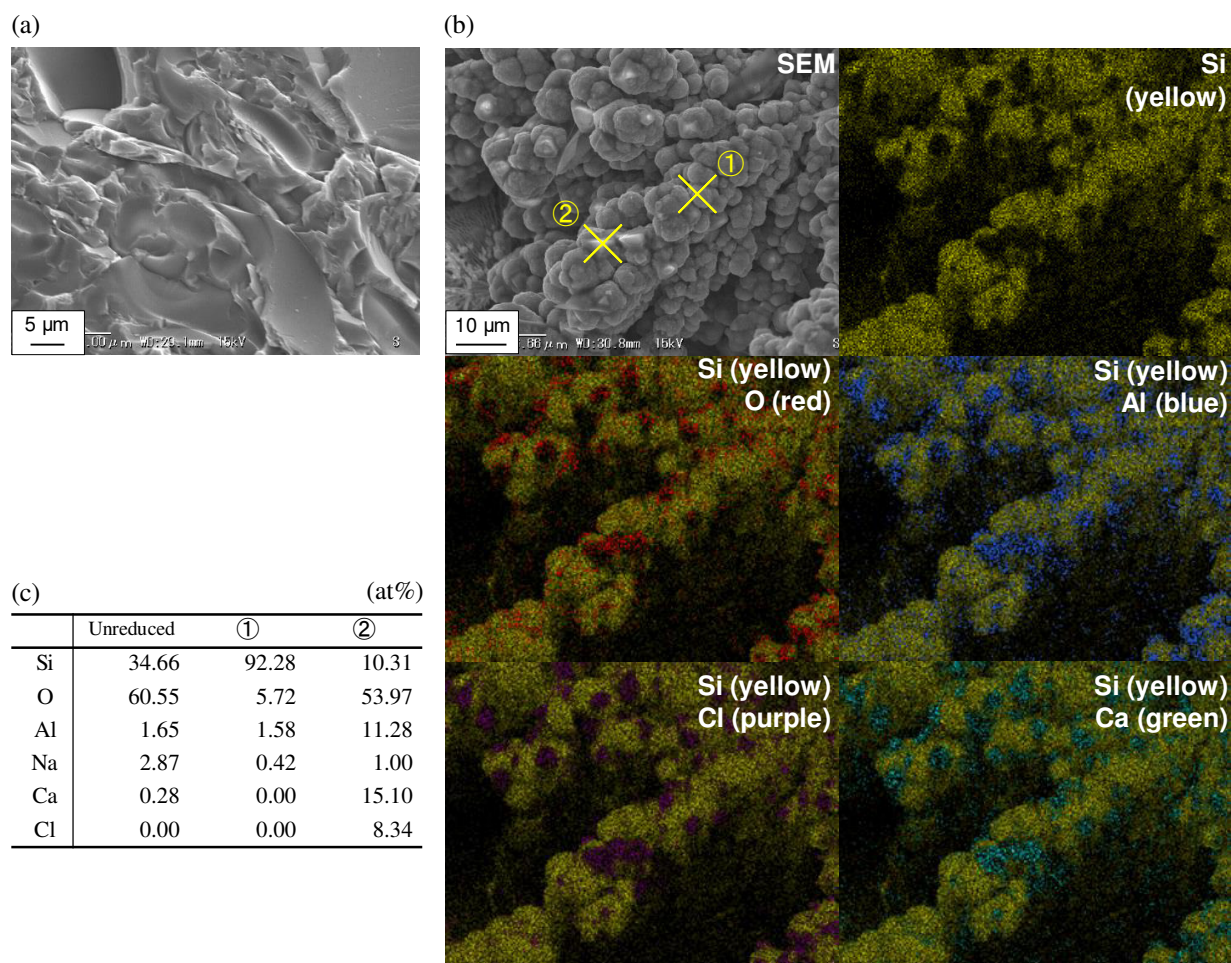


Figure 3-13 (a) SEM image of unreduced borosilicate glass. (b) SEM image and EDX maps for Si, (Si + O), (Si + Al), (Si + Cl) and (Si + Ca) of sample B-2 reduced at 0.9 V vs. Ca^{2+}/Ca for 30 minutes in molten CaCl_2 at 1123 K. (c) EDX analysis result for the unreduced borosilicate glass and the reduced borosilicate glass at point 1 and 2 indicated in (b).

Figure 3-13 shows (a) a SEM image of the unreduced borosilicate glass, (b) SEM image and EDX mapping results for the reduction products obtained by the electrolysis at 0.9 V for 30 minutes, and (c) the EDX analysis results for the two specified points in the figure. Following electrolytic reduction, the flat morphology of the original borosilicate glass changes to a granular one with a diameter of 1~10 μm . The different morphology from the previously reported result for silica glass, in which Si wires or Si columns with a diameter $\sim 1 \mu\text{m}$ were observed [11,15], might be attributed to the presence of boron oxide and aluminum oxide. As shown from EDX mapping results, the areas with high O concentration always contain Al, Ca, and Cl, suggesting that

aluminum oxide is not reduced at 0.9 V, and that calcium aluminate forms via the reaction with CaO in the molten salt. This explanation is consistent with the potential– pO^{2-} diagram for the Al–Ca–O–Cl system [16]. Here, the detected Cl is likely due to the complex compounds with calcium aluminate and $CaCl_2$. As for Na content, the dissolution of Na_2O into molten $CaCl_2$ is indicated because the Na concentration largely decreased both in the reduced area (point 1) and unreduced area (point 2) relative to the original value. Incidentally, the concentration of K in the original borosilicate glass was below the detection limit of EDX. Considering the thermodynamic calculation and the chemical similarity with Na, the behavior of K is believed to be the same as that of Na.

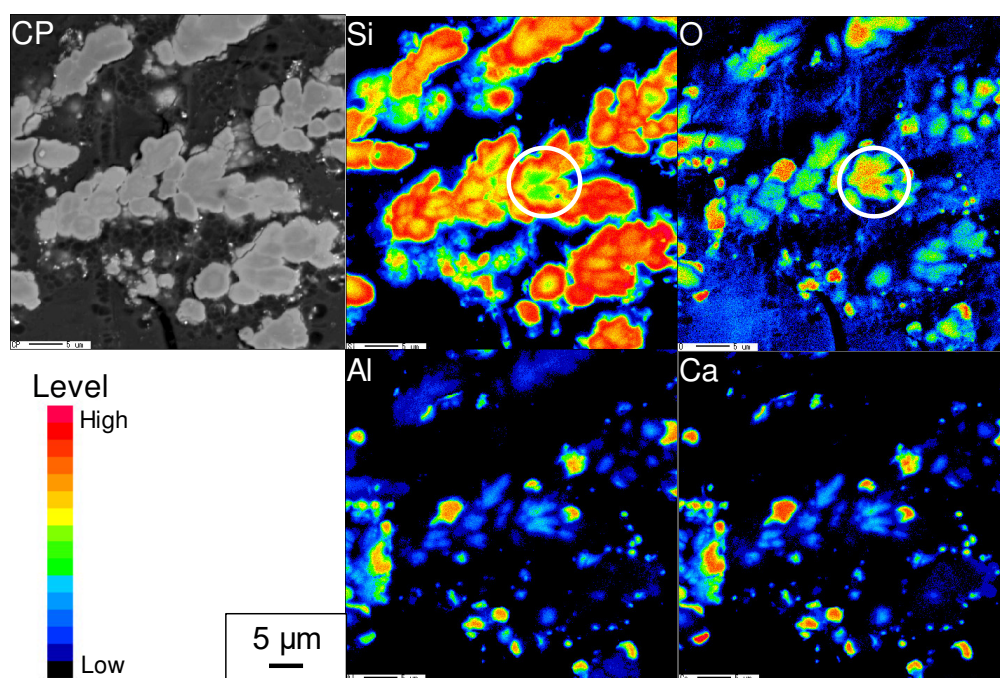


Figure 3-14 SEM/WDX cross-sectional maps of products obtained by the electrochemical reduction of a sealed borosilicate glass electrode at 0.9 V vs. Ca^{2+}/Ca for 30 min in molten $CaCl_2$ (White circle shows the inside of the grains including Si, Al, Ca, and O).

The reduction behavior of Al_2O_3 was investigated by SEM/WDX cross-sectional mappings of the products obtained at 0.9 V for 30 min (Figure 3-14). The result agrees well with previously reported surface SEM/EDX mappings where most of the O-rich areas coincide with the Al-rich areas and Ca-rich areas (Figure 3-13). This result indicates that Al_2O_3 is not reduced and that calcium aluminates are formed both in the bulk and on the surface of the reduced products. In the potential- $p\text{O}^{2-}$ diagram for the Al-Ca-O-Cl system (Figure 3-14), the conditions for no reduction of Al_2O_3 and the formation of calcium aluminates is found to be the region where $p\text{O}^{2-} < 4.33$.

3.3.6 Interpretations of the behavior of each element

Figure 3-14 shows that several regions inside the granules produced contain Si, Al, Ca, and O (one such region is shown as a white circle in Figure 3-14). This result is interpreted as being due to a mixture of reduced silicon and unreduced calcium aluminates, which agrees with the previous discussions.

The reaction conditions including the $p\text{O}^{2-}$ value can be deduced from the experimental results. Figure 3-14(a) shows the superimposed potential- $p\text{O}^{2-}$ diagrams for the Si-Ca-O-Cl, B-Ca-O-Cl, and Al-Ca-O-Cl systems. In this diagram, the common region stable for calcium aluminates (yellow), Si (red), and B (blue) exists. The common region for the obtained species is shown in yellow in Figure 3-14(b). At 0.9 V, the $p\text{O}^{2-}$ values for the formation of Si and B are larger than 2.95 and 2.62, respectively. For the formation of calcium aluminates, the $p\text{O}^{2-}$ value is smaller than 4.33. To summarize, the reduction product in this study was formed in the range $2.95 < p\text{O}^{2-} < 4.46$. This $p\text{O}^{2-}$ range is smaller than the reported $p\text{O}^{2-}$ value of 5.5 for the electrochemical reduction of SiO_2 in molten CaCl_2 [5]. One of the reasons for the decreased $p\text{O}^{2-}$ value is the emission of O^{2-} ions by the dissolution of Na_2O . Although calcium silicates are formed by the reaction with CaO in the melt as an intermediate in the reduction of SiO_2 [5], they are then reduced

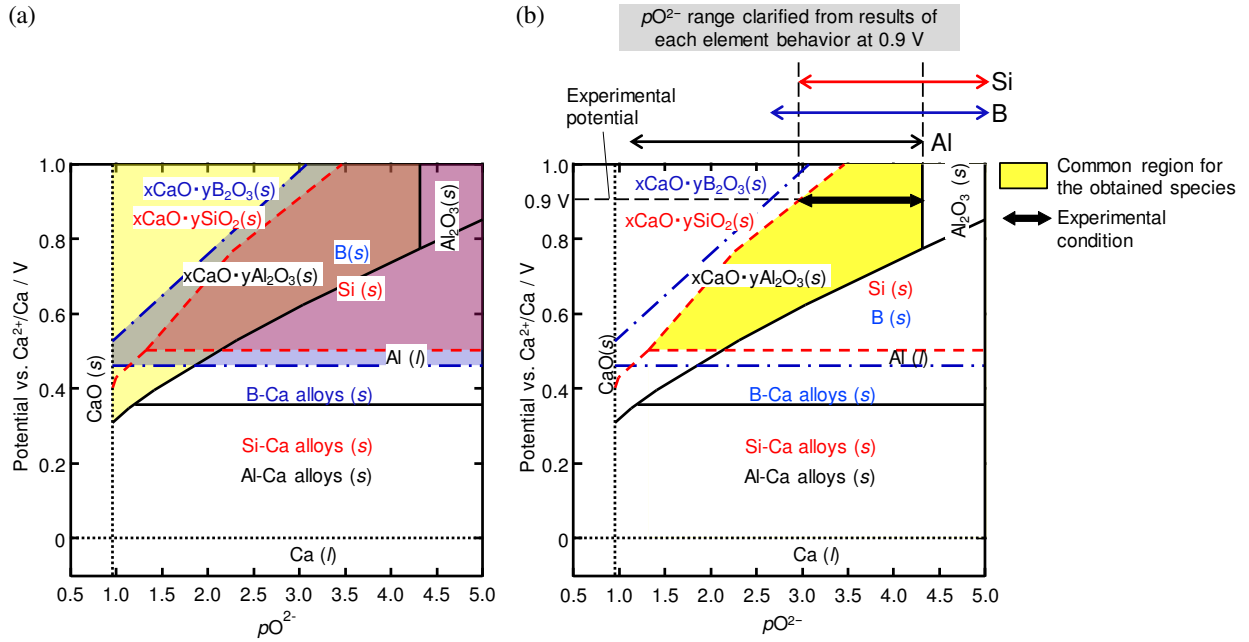


Figure 3-15 Superimposed potential- $p\text{O}^{2-}$ diagrams for the Si-, B-, and Al-Ca-O-Cl systems in molten CaCl_2 at 1123 K for the low $p\text{O}^{2-}$ region (red dashed line: boundary between Si and other compounds in Si-Ca-O-Cl system, blue dash-dot line: boundary between B and other compounds in B-Ca-O-Cl system, black line: boundary between Al and other compounds in Al-Ca-O-Cl system). (a) The stable region for Si, B, and calcium aluminates. (b) Common region for the obtained species and $p\text{O}^{2-}$ range obtained from experimental results of each element behavior at 0.9 V.

to Si to produce O^{2-} ions at 0.9 V. B_2O_3 will have a similar reduction pathway to that of SiO_2 . Conversely, calcium aluminates are not reduced in this $p\text{O}^{2-}$ range, and the CaO formed both by the dissolution of Na_2O and the reduction of SiO_2 and B_2O_3 will react with Al_2O_3 . Therefore, the value of $p\text{O}^{2-}$ remains around 4.33 where the boundary between CaAl_4O_7 and Al_2O_3 exists.

Based on the results obtained throughout this study, including the potential- $p\text{O}^{2-}$ diagrams and characterizations of the products, the reaction mechanism and the behavior of each element during the reduction of borosilicate glass at 0.9 V are summarized as follows:

1. Dissolution of Na_2O and K_2O and emission of O^{2-} ions.
2. Phase separation of borosilicate glass.
3. Reduction of SiO_2 to Si *via* a $\text{Ca}_x\text{Si}_y\text{O}_z$ intermediate and B_2O_3 to B *via* a $\text{Ca}_x\text{B}_y\text{O}_z$ intermediate at 0.9 V.

4. Reaction of the more abundant O^{2-} ions with Al_2O_3 to form calcium aluminates.

Repetition of steps 1–4 leading to a pO^{2-} range of $2.95 < pO^{2-} < 4.33$.

3.4 Conclusion

The electrochemical reduction behavior of borosilicate glass with a composition of 80.8 wt% SiO_2 , 12.5 wt% B_2O_3 , 2.3 wt% Al_2O_3 , 4.0 wt% Na_2O , and 0.4 wt% K_2O was investigated in molten $CaCl_2$ at 1123 K.

Based on cyclic voltammogram comparisons between borosilicate and silica glasses, the reduction of oxides other than SiO_2 was determined for borosilicate glass.

In the potentiostatic electrolysis at 0.6 V (vs. Ca^{2+}/Ca) and 0.9 V, the reduction currents were larger for borosilicate glass compared to those of silica glass. The larger currents were explained by the faster reaction toward the inner glass, though the reduction rate in the surface direction was smaller than that of silica glass. The reduction of SiO_2 to crystalline Si and the reduction of B_2O_3 to B or B–Si compound were confirmed by XRD and XPS analyses. Raman spectrum analysis also shows the formation of B–Si bonds in a B-containing crystalline Si phase.

The granular morphology with 1–10 μm diameter was observed in the reduced area in the reduced borosilicate glass by SEM and the main component of granules was Si. According to the EDX and WDX analysis, Al_2O_3 was not reduced and calcium aluminate was formed. The results also indicated that the Na_2O component dissolved into the molten salt during electrolysis. The behavior of the K_2O component was considered to be the same as that of Na_2O , although the analysis could not be completed because of its low concentration.

The above results agree with the potential– pO^{2-} diagrams constructed from published thermodynamic data, in which the pO^{2-} range was indicated to stay at $2.95 < pO^{2-} < 4.33$ as a result of the dissolution of Na_2O , the reduction of B_2O_3 and SiO_2 and the formation of calcium aluminates during the electrolysis at 0.9 V.

3.5 Reference list

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Chapter 4

Electrochemical reduction of Al_2O_3

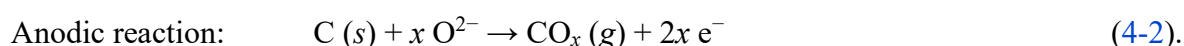
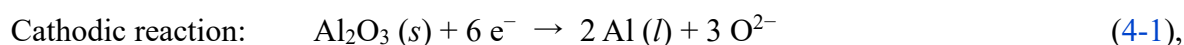
4.1 Introduction

Nuclear vitrified waste contains Al_2O_3 as the base glass component. Therefore, the clarification of the electrochemical reduction behavior of Al_2O_3 in molten CaCl_2 is important.

For the electrochemical reduction of Al_2O_3 , there have been several studies conducted in CaCl_2 -based melts [1–5]. Yan investigated the reduction of Al_2O_3 tube using a Nb box-type cathode in molten CaCl_2 – NaCl at 1173 K [1]. In this study, Al-rich Al–Ca alloy droplets with 84.9–98.4 at%Al were obtained. Yan and Fray also reported the electrochemical reduction of Al_2O_3 in CaCl_2 – LiCl at 973 K and CaCl_2 – NaCl at 1173 K [3]. They reported that calcium aluminate was formed as an intermediate product during the electrolysis. Xie *et al.* [2,4] reported that Al droplets were obtained by the electrochemical reduction of Al_2O_3 in molten CaCl_2 – NaCl at 823 K [2] and at 1073 K [4]. However, the purity of Al droplets was not clear. In all above studies, because they used a two-electrode system, the reaction mechanism including the relations between the electrode potential and the formation phase has not been clarified yet. Recently, Suzdaltsev *et al.* reported that Al_2O_3 powder was chemically reduced by electrochemically produced Ca^+ and Ca in CaCl_2 – CaF_2 melt at 1023 K [5]. However, the role and influence of F^- ions such as in the dissolution of Al_2O_3 to the melt, has not been understood well, and the obtained Al droplets contained Al–Ca alloys. Despite the extensive studies, the electrochemical reduction behavior of Al_2O_3 in pure molten CaCl_2 has not been identified.

In the present study, the author's group has selected CaCl_2 as a molten salt, owing to its

many desirable properties: high solubility of O^{2-} ions [6], low cost, and no emission of fluorocarbon gases. Compared with $CaCl_2$ – $NaCl$ and $CaCl_2$ – KCl , pure $CaCl_2$ has higher solubility of O^{2-} ions, which is kinetically advantageous for the electrochemical reduction of metal oxides. When carbon is used as an anode, the expected reactions for the production of Al metal from Al_2O_3 in molten $CaCl_2$ are:



The fundamental studies have been conducted as follows. First, the potential– pO^{2-} diagrams for the Al–Ca–O–Cl system in molten $CaCl_2$ at 1123 K were constructed from thermochemical data to predict and discuss the reaction products depending on activity of O^{2-} ions. (It was already conducted in Chapter 2.) Second, cyclic voltammetry was conducted to investigate the reduction behavior of Al_2O_3 , whereby the electrode potential was accurately controlled and measured with a three-electrode system by using a Ag^+/Ag reference electrode [7]. Third, Al_2O_3 powder and Al_2O_3 tubes were electrolytically reduced by potentiostatic electrolysis using Fe box-type and Mo box-type electrodes. Finally, based on the analysis results of the products and the potential– pO^{2-} diagrams, the reaction mechanisms of the electrochemical reduction of Al_2O_3 tube and powder were discussed.

4.2 Experimental

A schematic drawing of the experimental apparatus for molten $CaCl_2$ is shown in Figure 4-1. In an open dry chamber, 350 g of $CaCl_2$ (> 95.0 %, Wako Pure Chemical Industries, Ltd.) was used. The procedure of drying salt is the same as in Chapter 3. The experiments were conducted inside stainless steel inner and the Kanthal outer vessel at 1123 K under a dry Ar atmosphere.

Graphite counter electrode and Ag^+/Ag electrode were used in the experiment. Counter and reference electrode structure are described in the Chapter 3.

Three types of working electrodes, shown in Figure 4-2, were used depending on the purpose. An Al_2O_3 -sealed electrode was prepared by inserting a W rod (> 99.95 %, diameter: 2.0 mm, Nilaco Corp.) in an Al_2O_3 tube (99.6 %, o.d.: 3.0 mm, i.d.: 2.0 mm, Nikkato Corp.), as shown in Figure 4-2(a). An Fe box-type electrode (6 mm $\times$ 6 mm $\times$ 10 mm) was prepared with an Fe sheet (99.5%, thickness: 0.10 mm, Nilaco Corp.). After spot-welding of a Mo wire current lead (Figure 4-2(b)), approximately 100 mg of Al_2O_3 powder (99.9 %, particle size: 0.212–0.5 mm, Kojundo Chemical Lab. Corp.) was charged in the Fe box-type electrode. A Mo box-type electrode (12 mm

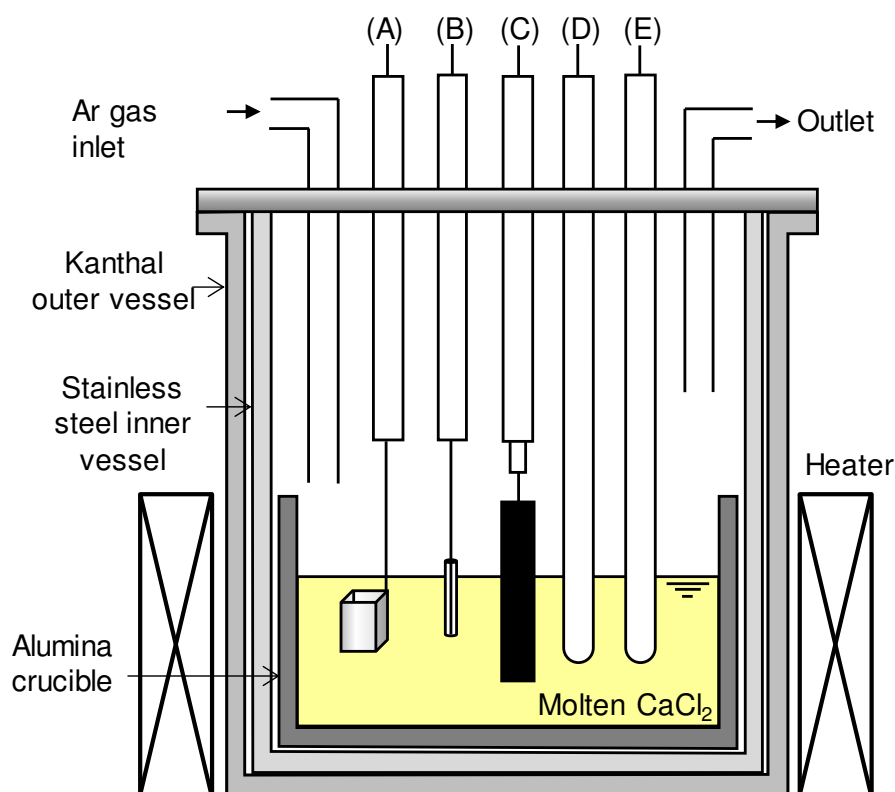


Figure 4-1 Schematic figure showing the experimental apparatus. (A) Working electrode (box electrode), (B) working electrode (Al_2O_3 -sealed electrode), (C) graphite counter electrode, (D) Ag^+/Ag reference electrode, and (E) thermocouple.

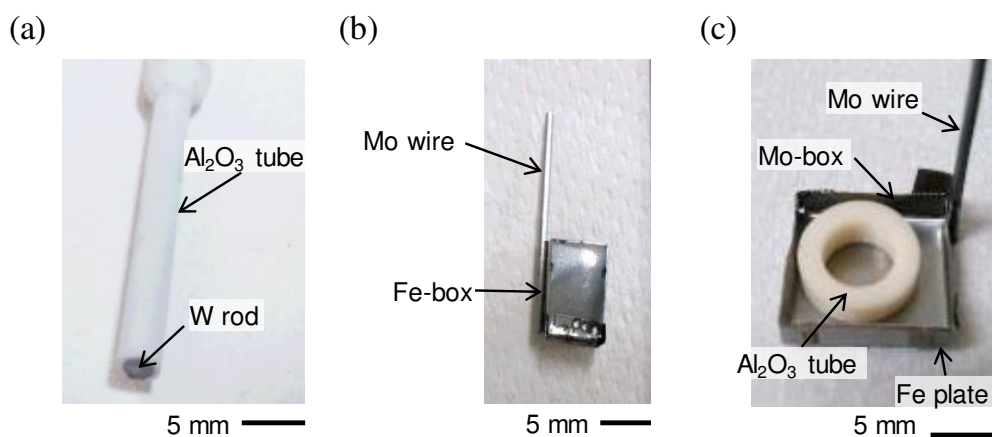


Figure 4-2 Photographs of the Al₂O₃ contacting electrodes. (a) Al₂O₃-sealed electrode, (b) Fe-box electrode (Al₂O₃ powder was contained), and (c) Mo-box electrode (Al₂O₃ tube was placed).

× 12 mm × 3 mm), shown in Figure 4-2(c), was fabricated from a Mo sheet (99.5%, thickness: 0.10 mm, Nilaco Corp.), for which small Fe sheets used to reinforce the corners of the box. The Mo box-type electrode was used for the reduction of an Al₂O₃ tube (99.6 %, o.d.: 10 mm, i.d.: 6 mm, Nikkato Corp.).

After the potentiostatic electrolysis, the Al₂O₃-sealed electrodes were rinsed with distilled water to remove the residual salts and dried at room temperature. Then, they were cut by a desktop abrasive cutting machine (RC-120, As One Corp.) into sections of approximate length 10 mm. The samples prepared with Fe-box and Mo-box type electrodes were washed with anhydrous ethylene glycol (99.5%, Wako Pure Chemical Industries Ltd.) using an ultrasonic washing machine and rinsed with anhydrous acetone (99.5%, Wako Pure Chemical Industries Ltd.). Ethylene glycol was used because it dissolves CaCl₂ without reacting with Ca alloy. X-ray diffractometry (XRD; Rigaku, Ultima IV, Cu-K α ray, $\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA) was used for sample identification. The samples were observed by using an optical digital microscope (Dino Lite PRO Polarizer DILITE30 AM-413ZT, Sanko Co., Ltd.) and scanning electron microscopy (SEM; VE-8800, Keyence Corp.). The elemental composition of the sample surfaces was analyzed

by energy-dispersive X-ray spectroscopy (EDX; EDAX Genesis APEX2, AMETEK Co., Ltd., accelerating voltage: 15 kV). The aluminum droplets obtained by the electrolysis were dissolved into 0.528 mL of 30 wt% HCl solution. Then, pure water was added to a total volume of 50 mL. Inductively coupled plasma atomic emission spectrometry (ICP-AES; SPECTRO Blue, Hitachi High-Tech Science Group) was used for the elemental analysis.

4.3 Results and discussion

4.3.1 Cyclic voltammetry

The reduction behavior of Al_2O_3 in the three-phase zone is investigated by cyclic voltammetry using an Al_2O_3 -sealed electrode. Figure 4-3 shows cyclic voltammograms (CVs) measured in a potential range of 0.2–1.9 V (vs. Ca^{2+}/Ca) for five consecutive cycles. The apparent current density is calculated by using the cross-sectional area of the W rod (dia. 2 mm). In the first cycle, when the scan starts from the rest potential (*ca.* 1.7 V) in the negative direction, the reduction current sharply increases from 0.6 V and gives a peak at *ca.* 0.45 V. According to the potential– $p\text{O}^{2-}$ diagram (Figure 2-5), the reaction is expected to be the electrochemical reduction of Al_2O_3 to Al metal:



The cathodic current further increases from 0.35 V, which would correspond to the formation of Al_2Ca :



In addition, the current increases with the cycle number, which indicates an increase in the effective reaction zone of conductor/ Al_2O_3 /molten salt by the formation of conductive products, such as metallic Al and Al_2Ca .

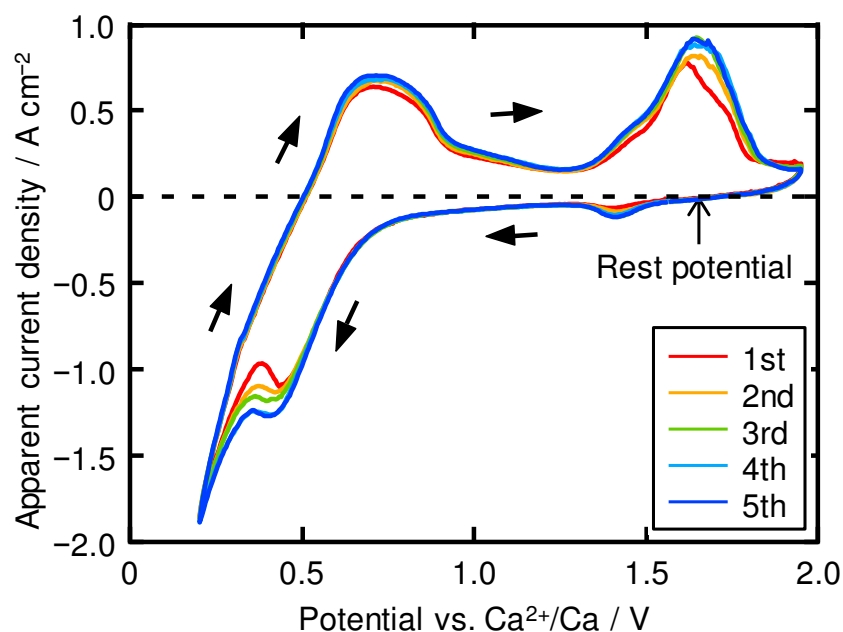


Figure 4-3 Cyclic voltammograms for an Al_2O_3 -sealed electrode in molten CaCl_2 at 1123 K. Scan rate: 50 mVs^{-1} . Switching potential: 0.20 V.

4.3.2 Potentiostatic electrolysis of Al_2O_3 -sealed electrodes

The reduction of Al_2O_3 is investigated by potentiostatic electrolysis of Al_2O_3 -sealed electrodes at 0.30 V for 30 and 60 min. Microscope images of the samples before and after electrolysis are shown in [Figure 4-4](#). After 30 min, there are traces of reduction at the Al_2O_3 tube near the W rod. In the case of 60 min, the traces of reduction have spread in the outer direction. These results indicate that the reduction starts in the three-phase zone of Al_2O_3 , the conductive W rod, and molten CaCl_2 . From an EDX analysis of the 60-min sample, the composition of the reacted area is O 20 at%, Al 60 at %, which confirms the electrochemical reduction of Al_2O_3 .

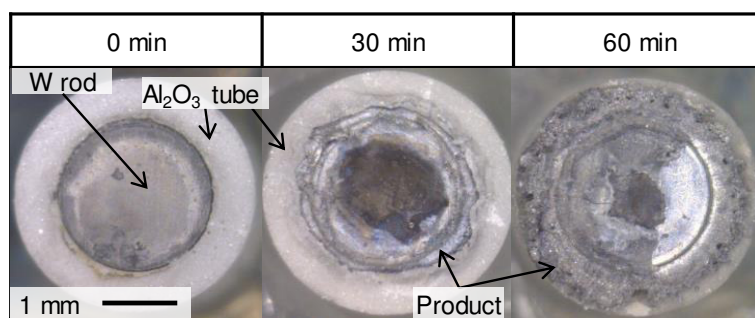


Figure 4-4 Optical images of the Al_2O_3 sealed electrodes before and after the potentiostatic electrolysis at 0.30 V for 0, 30, and 60 min in molten CaCl_2 at 1123 K.

4.3.3 Potentiostatic electrolysis of Al_2O_3 powder using Fe-box type electrodes

With reference to the CV results, potentiostatic electrolysis of Al_2O_3 powder is conducted at 0.50, 0.40, 0.30, 0.25, and 0.20 V for 6 h using Fe-box electrodes to investigate the potential dependence of reaction. Figure 4-5(a) shows the current–time curves during the electrolysis. Larger cathodic currents are observed at more negative potentials. Cross-sectional optical images of the obtained samples are shown in Figure 4-5(b). The powders are found at the bottom and the solidified CaCl_2 are found above the powders in the Fe-box electrodes. The color of the powder changes from white to black at 0.40 V, to greenish-brown at 0.30 V and 0.25 V, and to metallic silver at 0.20 V.

XRD patterns of the powders are shown in Figure 4-6. The distinct peak pattern for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is observed for the samples at 0.25, 0.30, 0.40, and 0.50 V. Yan and Fray also reported that $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ was formed in the electrochemical reduction of Al_2O_3 in CaCl_2 -based melt [3]. The patterns for 0.30, 0.40, and 0.50 V indicate the existence of unreacted Al_2O_3 , where the peak intensities are smaller at more negative potentials. For the sample at 0.20 V, only the Al_2Ca phase is confirmed. Incidentally, the inner surface of the Fe-box electrode had changed to Al_5Fe_2 (PDF # 00-047-1435) after electrolysis of Al_2O_3 powder at 0.4 V for 12 h, which is confirmed by its appearance and XRD analysis (Figure 4-7). Since the Fe-box alloyed with the produced Al, the

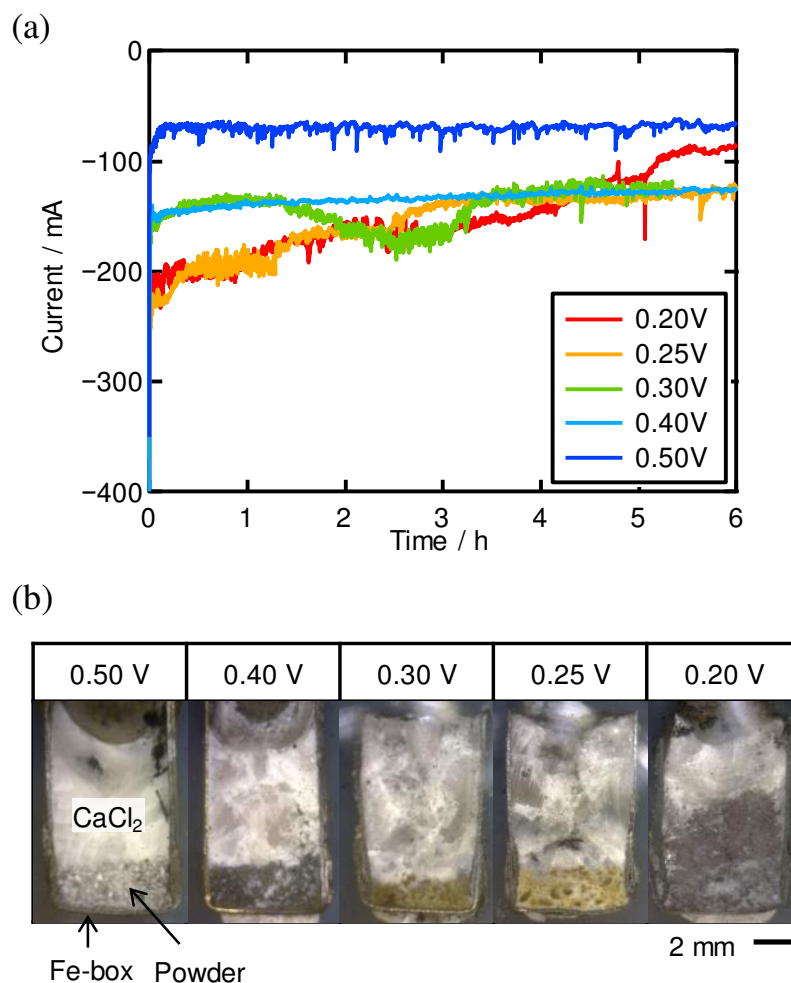


Figure 4-5 (a) Current–time curves during the potentiostatic electrolysis of the Fe-box electrodes containing Al₂O₃ powder at 0.50, 0.40, 0.30, 0.25, and 0.20 V for 6 h in molten CaCl₂ at 1123 K. (b) Cross-sectional optical images of the samples obtained by the potentiostatic electrolysis.

Al₅Fe₂ formed at the surface. The more internal parts of Fe walls may have contained other Al–Fe alloy phases with higher Fe content. However, they could not be detected by XRD due to the limited penetration depth of X-ray.

Ca₁₂Al₁₄O₃₃ has been reported to form free electrons in the cage framework of a crystal structure by a deoxidation reaction, showing a green color owing to the transition of free electrons to the conduction band and metallic conductivity at room temperature [8–12]. The samples obtained at 0.25 and 0.30 V, which are composed of Ca₁₂Al₁₄O₃₃, exhibit a greenish color,

suggesting that they have high conductivity after the electrochemical deoxidation. After Al_2O_3 powder in an Fe-box electrode is immersed in CaCl_2 for 6 h without electrolysis, the formation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is not confirmed. Thus, the $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ at 0.25 and 0.30 V is considered to be formed by the reaction of Al_2O_3 , Ca^{2+} , and electrochemically formed O^{2-} ions.

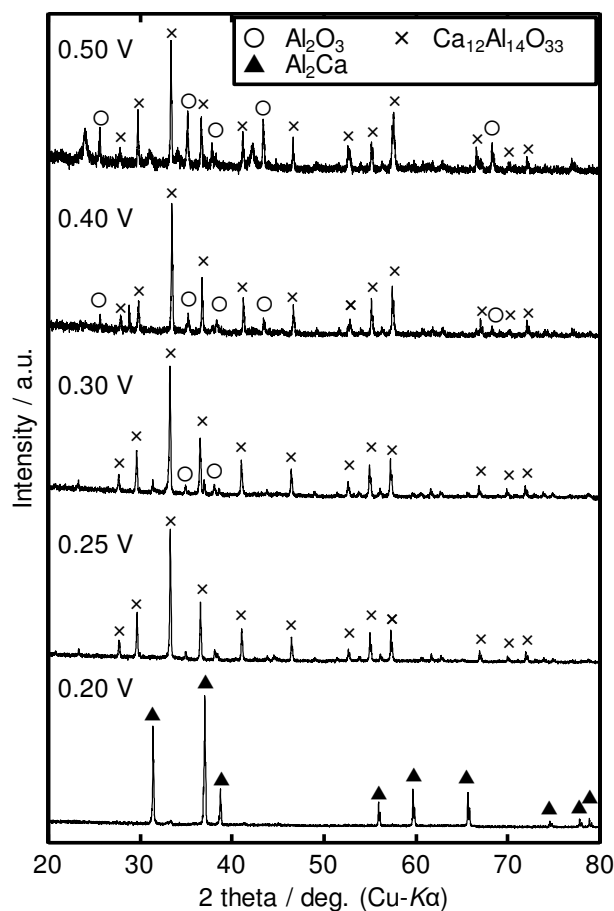


Figure 4-6 XRD patterns of the samples obtained by the potentiostatic electrolysis of Al_2O_3 powder in the Fe-box electrodes at 0.50, 0.40, 0.30, 0.25, and 0.20 V for 6 h in molten CaCl_2 at 1123 K.

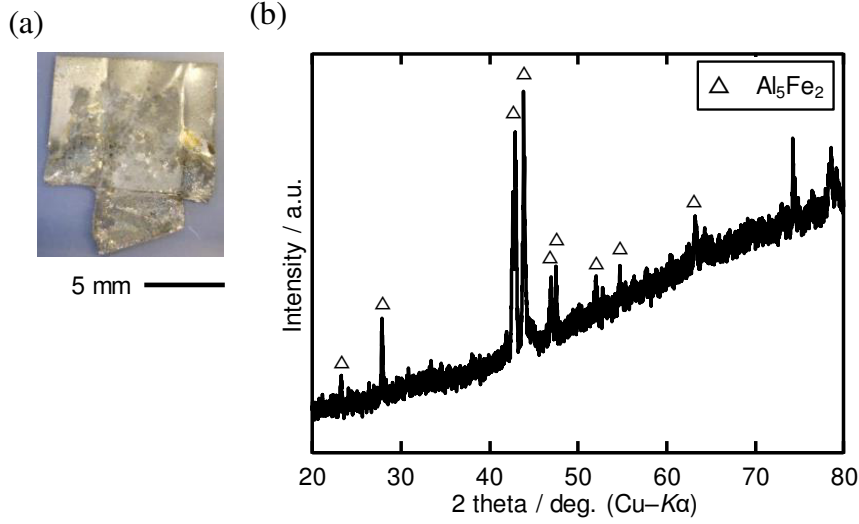
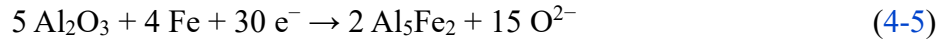


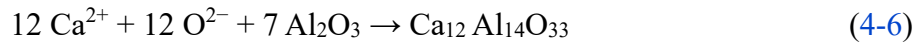
Figure 4-7 (a) Optical image and (b) XRD pattern of the Fe-box electrode after the potentiostatic electrolysis of Al_2O_3 powder at 0.40 V for 12 h in molten CaCl_2 at 1123 K.

To summarize these results, the mechanism of the reduction of Al_2O_3 powder in an Fe-box electrode is described as follows.

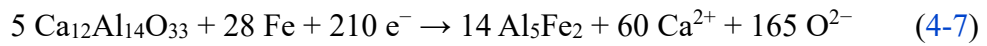
- (1) At first, Al_2O_3 in contact with the Fe-box electrode is reduced to Al_5Fe_2 alloy.



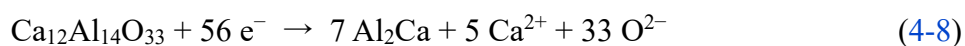
- (2) In the vicinity of the reduced Al_2O_3 powder, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is formed by the reaction of Al_2O_3 , Ca^{2+} , and the electrochemically produced O^{2-} ions.



- (3) The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ near the Fe-box electrode is reduced to form Al_5Fe_2 alloy.



- (4) When the electrode potential is below 0.20 V, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is electrochemically reduced to form Al_2Ca .



Considering that the obtained phases are $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and Al_2Ca alloy for the Fe-box electrodes, the concentration of O^{2-} ions in the three-phase zone of Al_2O_3 /molten salt/conductor is high ($p\text{O}^{2-} < 1.41$) during the electrolysis. The high concentration of O^{2-} ions is believed to be brought about by the stagnation of O^{2-} ions in the Al_2O_3 powder. The diffusion of O^{2-} ions from the electrochemical reaction interface to the bulk molten salt is not easy, owing to the long diffusion paths passing through the gaps between the Al_2O_3 particles. In order to obtain Al metal with low Ca content, the concentration of O^{2-} ions must be kept low ($p\text{O}^{2-} > 2.86$ for Ca content < 0.1 at%) To realize this, the diffusion of O^{2-} ions from the reaction interface to the bulk molten salt has to be facile. For this purpose, a new electrode structure, in which a dense Al_2O_3 tube is placed on a flat metal plate, is considered to be effective.

4.3.4 Potentiostatic electrolysis of Al_2O_3 tube in Mo box-type electrode

On the basis of the above considerations, the electrochemical reduction of Al_2O_3 tube is carried out using a Mo-box electrode with a wide bottom and a shallow depth (Figure 4-2(c)). Mo has been used instead of Fe, because it is not easily alloyed with Al.

Figure 4-8 shows a current–time curve during the potentiostatic electrolysis at 0.25 V for 12 h. A nearly constant current of -200 mA is observed. Figure 4-9(a) shows an optical image of the sample after the electrolysis. Black products are found around the Al_2O_3 tube. After washing the sample with ethylene glycol (Figure 4-9(b)), evident decreases in height and wall thickness are observed for the Al_2O_3 tube. Moreover, metallic droplets with an approximate maximum diameter of 3 mm are obtained from the bottom of the crucible (Figure 4-9(c)). The total mass of the droplets is 32 mg. Figure 4-10 shows an XRD pattern of the droplets, which confirms the formation of Al metal. An ICP-AES analysis of the obtained Al droplets reveals that the composition is 95.4–98.0

at% Al and 2.0 at%–4.5 at% Fe. The concentrations of Ca and Mo are less than the detection limit. In this experiment, the level of detection limit for ICP-AES is $1\text{--}2\times 10^{-2}$ at %. The current efficiency is calculated to be approximately 50% from the mass loss of the Al_2O_3 tube, 605 mg, and the charge during the electrolysis, 3431 C. The background current of the Mo-box electrode is likely the main reason for the low efficiency. In addition, formation of dissolved Ca in molten CaCl_2 is another cause of the low current efficiency by inducing shuttle current between the anode and the cathode; the solubility of metallic Ca in molten CaCl_2 is reported to be *ca.* 3 mol% at 1123 K [13]. The black deposits in the Mo-box electrode are identified as Al_2Ca by XRD analysis. The Al_2Ca phase is considered to be precipitated from liquid Al–Ca alloy upon cooling.

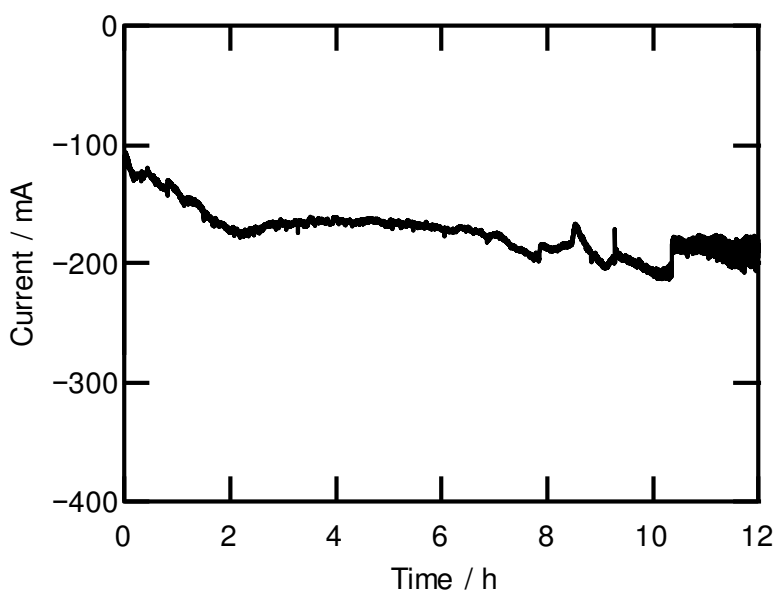


Figure 4-8 A current–time curve during the potentiostatic electrolysis of Al_2O_3 tube in the Mo-box electrode at 0.25 V for 12 h in molten CaCl_2 at 1123 K.

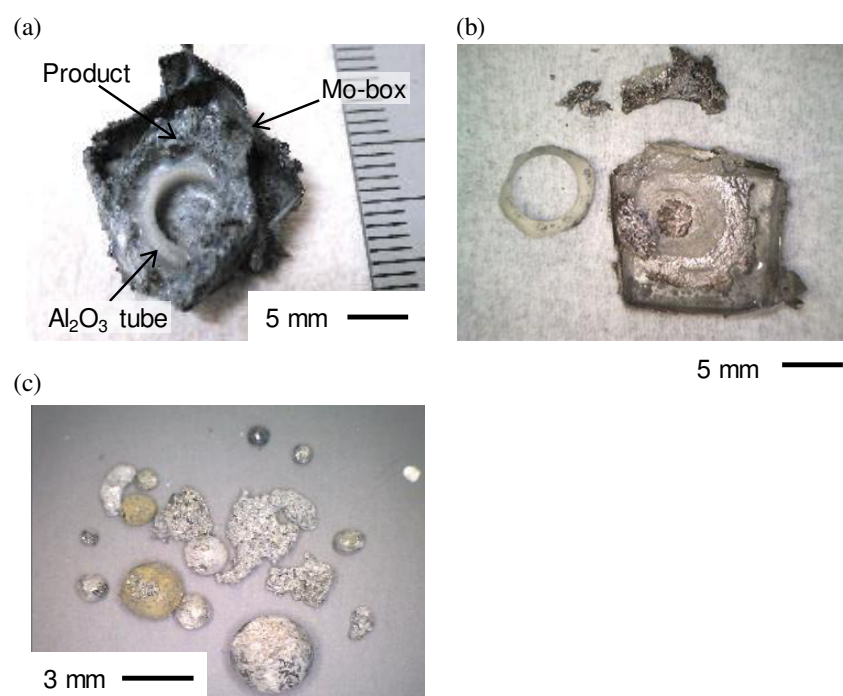


Figure 4-9 Optical images after the potentiostatic electrolysis of the Al_2O_3 tube in the Mo-box electrode at 0.25 V for 12 h in molten CaCl_2 at 1123 K (a) before and (b) after washing the Mo-box electrode, and (c) metal droplets obtained from the bottom of the crucible after the electrolysis.

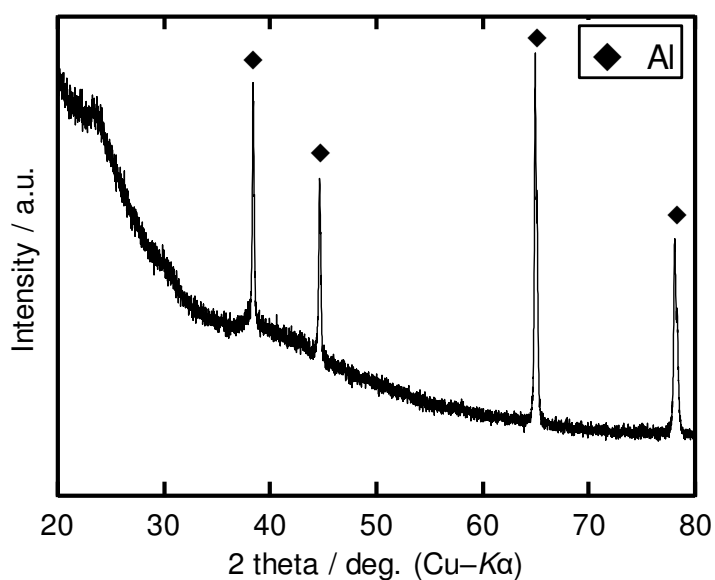


Figure 4-10 XRD pattern of the metal droplets obtained from the bottom of the crucible after potentiostatic electrolysis of the Al_2O_3 tube in the Mo-box electrode at 0.25 V for 12 h in molten CaCl_2 at 1123 K.

The above results have demonstrated that the new electrode structure is effective. Figure 4-11 compares the diffusion paths of O^{2-} ions for Al_2O_3 powder and Al_2O_3 tube. Electrochemical reduction of Al_2O_3 occurs at the three-phase zone to produce O^{2-} ions, which decrease the value of pO^{2-} . In the case of powder, the diffusion of O^{2-} ions is slow due to the small space among particles (left in Figure 4-11), which causes the very low pO^{2-} in the three-phase zone. The deeper color means the low pO^{2-} region, *i.e.*, the high O^{2-} ion concentration region. On the contrary, for the tube, the facile diffusion of O^{2-} ions enables the higher pO^{2-} in the three-phase zone. According to the potential- pO^{2-} diagram, the production of Al metal is possible only when the pO^{2-} is not very low. Thus, even for Al_2O_3 powder, the production of Al metal is expected by using a larger particle size and/or by performing agitation.

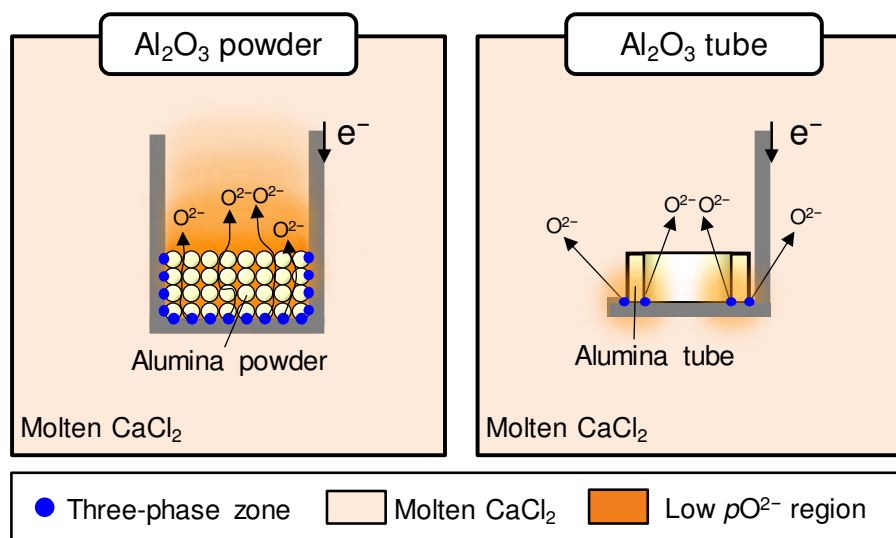


Figure 4-11 Difference in diffusion paths between the electrolysis of Al_2O_3 powder and tube.

4.4 Conclusion

The electrochemical reduction of solid Al_2O_3 has been investigated in molten CaCl_2 at 1123 K. Cyclic voltammetry using an Al_2O_3 -sealed electrode indicates that the reduction of Al_2O_3 proceeds at potentials more negative than 0.6 V. When Al_2O_3 powder is electrolyzed in an Fe-box electrode, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ is formed at 0.25 and 0.30 V, and Al_2Ca is formed at 0.20 V. However, Al droplets are obtained from the bottom of a crucible by the electrolysis of an Al_2O_3 tube in a Mo-box electrode at 0.25 V. The difference in the reduction behavior is explained by the diffusivity of O^{2-} ions from the reaction interface to the bulk molten salt and thermodynamic considerations using the potential– $p\text{O}^{2-}$ diagrams.

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Chapter 5

Electrochemical reduction of simplified simulants

5.1 Introduction

The electrochemical behavior of LLFPs during the electrolysis of the vitrified waste in molten CaCl_2 must be clarified to develop this process because the occurrence of electrochemical reduction and chemical reaction depends on the stability of the oxides, electrolysis potential, electrolysis temperature, and concentration of O^{2-} ions in the molten salt. In Chapter 3, the electrochemical reduction of borosilicate glass composed of SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , and K_2O was investigated using Pyrex[®] and Tempax[®] glasses as model glasses for the real vitrified wastes. The main component (SiO_2) was reduced to crystalline Si after potentiostatic electrolysis at 0.9 V vs. Ca^{2+}/Ca for 30 min. Al_2O_3 was not reduced but was converted to calcium aluminates. The reduction of B_2O_3 and the dissolution of Na_2O were also indicated. The electrochemical behavior of the constituent elements, i.e., Si, B, Al, Na, and K, agreed with the potential– $p\text{O}^{2-}$ diagrams constructed from the thermodynamic data for these species. The $p\text{O}^{2-}$ range was found to be 2.95–4.33 during electrolysis at 0.9 V. However, as shown in [Table 1-4](#) and [Table 1-5](#), vitrified waste has a different composition from that of Pyrex[®] glass (a typical borosilicate glass).

In this chapter, the author used two vitrified waste simulants. As shown in [Table 1-5](#), simulant 1 contains only the glass components (SiO_2 , B_2O_3 , Na_2O , Al_2O_3 , CaO , Li_2O , and ZnO) and has a similar composition to that of vitrified waste. Simulant 2 was prepared by adding LLFP oxides (ZrO_2 , Cs_2O , PdO , and SeO_2) to simulant 1. The softening points of two simulants (863–873 K) are much lower than that of Pyrex[®] glass (1093 K) and the electrolysis temperature (1103

K). Here, the softening point is defined as the temperature where the viscosity is $10^{7.5}$ dPa s [1]. Thus, the author improved the experimental method to avoid the fusion of the simulant powder during the electrolysis. To be precise, the author prepared pellets consisting of the simulant powder and CaCl_2 powder. Using this method, the three-phase glass/ CaCl_2 /conductor boundary was successfully maintained, facilitating the electrochemical reaction.

In the same manner as the previous study of borosilicate glass, potential– $p\text{O}^{2-}$ diagrams were constructed before the experiment to predict the behavior of each element in the simulants, shown in Chapter 2. Then, simulant 1 was electrochemically reduced in molten CaCl_2 and characterized by SEM/EDX and XRD analyses. Finally, immersion and electrolysis experiments were carried out for simulant 2. The samples were characterized by XRD, ICP-AES and ICP-mass spectrometry (MS). The composition of the molten salts after the experiments were also analyzed by ICP-AES/MS.

5.2 Experimental

Simulants 1 and 2 were synthesized by Nihon Horo Yuyaku Co. Ltd. Their compositions in Table 1-5 are target values. The author checked the compositions of simulant 2 by ICP-AES/MS (ICP-MS, 7700x, Agilent Technologies, Inc.). The analyzed composition, which is listed in Table 5-1, is basically similar with the target one. A certain degree of difference is found for Si probably because HF solutions with high Si concentration were introduced to the ICP-AES analyzer. In the present study, however, high accuracy is not necessary for Si because the behavior of Si is not a main theme here. On the other hand, certain discrepancies for the important LLFP elements, Pd, Cs, and Se could be problems. The analyze value of 0.24 for Pd is about half of the target one of 0.50. According to the glass supplier, their analyzed value for Pd by ICP-AES is 0.77. These large discrepancies are explained by the nonuniform distribution of Pd in the glass. The raw material of PdO is believed to decompose into Pd and coagulate during the synthesis process of simulant 2. Nevertheless, in terms of results, such nonuniformity is not a problem in the present study because,

as to be described later, Pd always remains in the solid products after the experiments. For Cs and Se, the analyzed values (0.60 for Cs and 0.04 for Se) are smaller than the target ones (1.0 for Cs and 0.1 for Se). According to the glass supplier, their analyzed value for Cs by atomic absorption spectroscopy is 0.84 and the value for Se by ICP-AES is 0.05. Since the similar analyzed values have been obtained by the authors and the suppliers, part of Cs_2O and SeO_2 possibly has evaporated during the synthesis process of simulant 2. The evaporation seems to be reasonable considering the stability and vapor pressure of Cs_2O (also Cs_2O_2 and CsO_2) and SeO_2 at high temperature.

The detail of the analysis method is described later. [Figure 5-1\(a\)](#) shows a schematic of the experimental apparatus. For the experiment, 450 g of CaCl_2 (> 95.0%, Wako Pure Chemical Industries, Ltd.) was crushed in an open dry chamber and transferred to an alumina crucible (o.d. 90 mm, height 140 mm, purity 99%, AS ONE Corp.). The procedure of drying salt is the same as in Chapter 3. The experiments were conducted inside the quartz glass vessel at 1103 K in a dry Ar atmosphere.

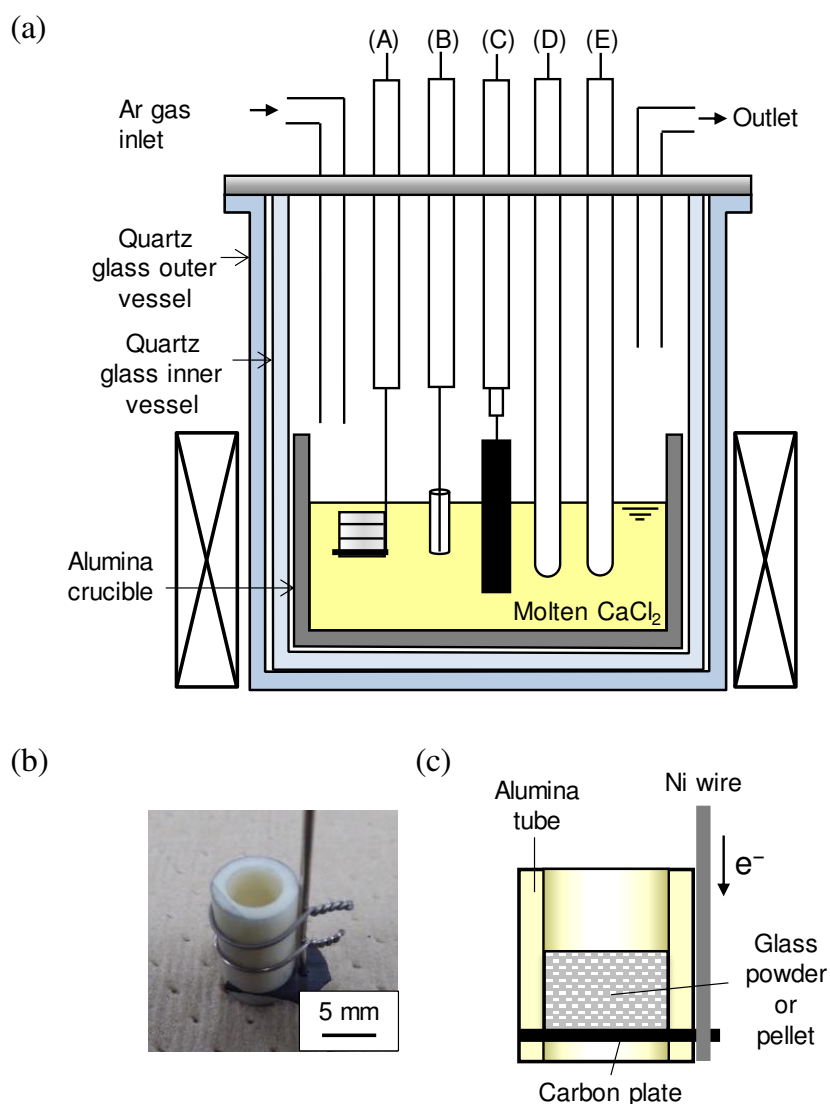


Figure 5-1 (a) Schematic figure showing the experimental apparatus. (A) Working electrode (small crucible), (B) working electrode (glass-sealed electrode), (C) graphite counter electrode, (D) Ag^+/Ag reference electrode, and (E) thermocouple. (b) A photograph and (c) schematic figure of the cross-section of the small crucible.

Electrochemical measurements are the same as in Chapter 3. Graphite counter electrode and Ag^+/Ag electrode were used in the experiment. Counter and reference electrode structure are described in the Chapter 3. For the electrochemical measurements, a glass-sealed electrode was prepared to use as the working electrode. Stainless steel (SS 430, dia. 1.2 mm, coefficient of linear thermal expansion: $104 \times 10^{-7} \text{ K}^{-1}$, Composition: C < 0.12 wt%, Si < 0.75 wt%, Mn < 1.00 wt%,

P < 0.04 wt%, S < 0.03 wt%, Cr 16.00–18.00 wt%, Nippon Seisen Co., Ltd.) was selected for the sealed metal rod because of its similar thermal expansion to that of the simulant 1 (composition shown in Table 1-5, coefficient of linear thermal expansion: $89.6 \times 10^{-7} \text{ K}^{-1}$, Nihon Horo Yuyaku Co., Ltd.). The stainless-steel rod was sealed in the melted simulant 1 under an Ar atmosphere at 1123 K by the dipping method (shown in Figure 5-2). After cooling to ambient temperature, the electrode was cut vertically by a desktop abrasive cutting machine and polished with sandpaper to prepare the three-phase interface (glass/CaCl₂/conductor) at the bottom and sides of the electrode. For the cyclic voltammetry measurements, the measurements started immediately after the immersion of the electrode in the melt to prevent the deformation of the electrode.

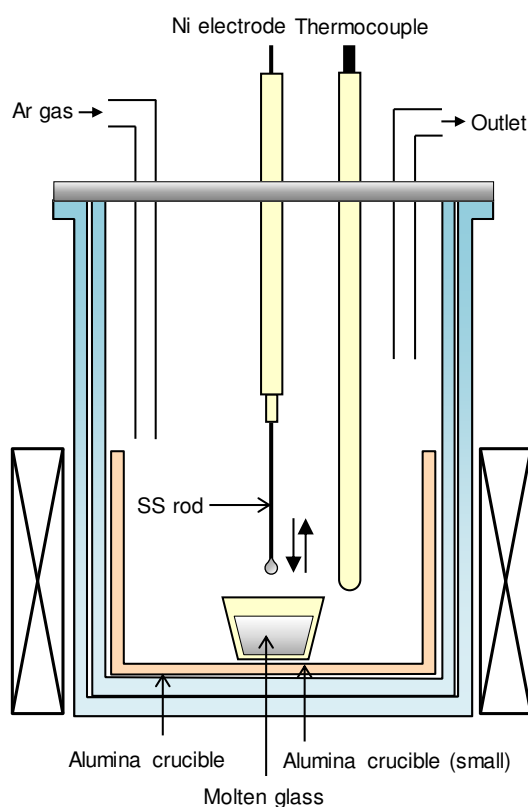


Figure 5-2 Schematic figure of experimental apparatus to fabricate a glass-seal electrode by the dipping method.

For the potentiostatic electrolysis, the small crucible electrodes shown in [Figure 5-1\(b\)](#) and (c) were used [2]. The small crucible electrode was prepared by cutting an Al_2O_3 tube (o.d. 8 mm, i.d. 5 mm, height 10 mm, 99.6%, Nikkato Corp.) and inserting a carbon plate (10 mm $\times$ 10 mm $\times$ 0.5 mm, 99.5%, Nilaco Corp.). A Ni wire (dia. 1.0 mm, 99%, Nilaco Corp.) was used as the current lead and connected to the carbon plate by threading it through a drilled hole (dia. 1.0 mm). Two Ni wires (dia. 0.5 mm, 99%, Nilaco Corp.) were wound around the Al_2O_3 tube to fix the Ni lead wire.

In the electrolysis of simulant 1, its powder was prepared by crushing in a mortar and sieving to the size of 0.1–0.212 mm. CaCl_2 grains were also crushed and sieved into powder (< 0.212 mm) in the same manner. The mixed powder of the simulant and CaCl_2 was charged in a small crucible in the open dry chamber. The ratio of the simulant and CaCl_2 was 1:0.2 by weight. The weight of the simulant used was around 50 mg. The Ni lead wire of the small crucible electrode was finally spot-welded to a Mo wire (dia. 1.0 mm, 99.95%, Nilaco Corp.). After potentiostatic electrolysis or immersion into the molten salt, the samples were taken out from the molten salt and rinsed with distilled water to remove the residual salts. After removing the Ni wires, the samples were cut by the desktop abrasive cutting machine to observe the reduction progress. The cross-section was observed using a digital optical microscope. The samples were first soaked in distilled water for longer than 8 h to remove the salt adhered to the samples. Then, the remaining solid was recovered from the solution by suction filtration and analyzed by XRD. The solid samples were further soaked in an 8% HCl solution for longer than 8 h and dried at 353 K, followed by instrumental analysis by XRD, SEM, and EDX.

In the case of simulant 2, the powder particles were smaller than 0.212 mm. First, a pellet (dia. 5 mm) was prepared from the mixed powder of simulant 2 and CaCl_2 (< 0.212 mm) in the open dry chamber. The ratio of simulant to CaCl_2 was 1:0.4 by weight, and the weight of simulant used was around 100 mg. A pellet was prepared under a pressure of around 0.3 MPa and was transferred to the small crucible electrode. Microscope observation and XRD analysis were

conducted on the electrolyzed samples. The molten salt was sampled for composition analysis by suction into a mullite tube (o.d.: 5 mm, i.d.: 3 mm, Nikkato Corp.) using a pipette bulb. The solidified salt collected in the tube was weighed in the open dry chamber. The solution prepared by dissolving the collected salt of around 3 g in 100 mL of aqueous 1 M HNO₃ solution was analyzed by ICP-AES and ICP-MS (7700x, Agilent Technologies, Inc.). The dissolution ratio α_{dis}^i of element i is defined as

$$\alpha_{\text{dis}}^i = \frac{c_{\text{MS}}^i \cdot m_{\text{solution}} \cdot \frac{M_{\text{MS}}}{m_{\text{MS}}}}{C_{\text{raw}}^i \cdot M_{\text{glass}}} \times 100 (\%), \quad (5-1)$$

where c_{MS}^i is the concentration of element i in the HNO₃ solution of molten salt, m_{solution} is the weight of solution, m_{MS} is the weight of sampled salt, M_{MS} is the total weight of molten salt in the experiment, C_{raw}^i is the concentration of element i in simulant, and M_{glass} is the total weight of the used simulant glass.

For the analysis of the solid product in the small crucible electrode, the solution prepared by dissolving the sample into either (HNO₃ + HCl) solution (both 5 M) or 10 M HF solution was analyzed. As a preliminary experiment, a suitable solution for quantitative analysis was chosen for each element, between (HNO₃ + HCl) and HF solutions, from the measured weight for the original simulant 2 (Table 5-1). To measure all the elements, two samples electrolyzed under the same experimental condition were dissolved in different solutions. Here, an HNO₃ solution was also added to HF solution for the dissolution of the reduced sample to oxidize Si. ICP-MS was used for the analysis of Pd, Cs, and Se. The remaining ratio α_{solid}^i of element i in the solid is defined as

$$\alpha_{\text{solid}}^i = \frac{c_{\text{glass}}^i \cdot m_{\text{solution}}}{C_{\text{raw}}^i \cdot m_{\text{glass}}} \times 100 (\%), \quad (5-2)$$

where c_{glass}^i is the concentration of element i in the solution of solid products collected from the

small crucible, and m_{glass} is the weight of the simulant glass in the small crucible before the experiment.

Table 5-1 The analyzed composition of simulant 2 by ICP-AES/MS. (HNO₃ + HCl) or HF solution was used to dissolve the glass. The adopted solution and composition are also listed.

Oxide	Measured composition (wt%)		Selected solution	Composition (wt%)
	HNO ₃ +HCl	HF		
SiO ₂	0.73	60.77	HF	60.77
B ₂ O ₃	13.29	18.32	HF	18.32
Na ₂ O	9.06	6.35	HNO ₃ +HCl	9.06
Al ₂ O ₃	4.03	1.36	HNO ₃ +HCl	4.03
Li ₂ O	3.19	2.15	HNO ₃ +HCl	3.19
ZnO	2.96	4.06	HF	4.06
PdO*	0.24	0.08	HNO ₃ +HCl	0.24
ZrO ₂	0.15	1.50	HF	1.50
Cs ₂ O*	0.60	-	HNO ₃ +HCl	0.60
SeO ₂ *	0.04	-	HNO ₃ +HCl	0.04
			Total	101.81

5.3 Results and discussion

5.3.1 Cyclic voltammetry

For the cyclic voltammetry (CV) measurements of simulant 1, the glass-sealed electrode was cut in half vertically, as shown in Figure 5-3(a). The reaction zone is located between the glass and the stainless-steel rod at the sides and bottom of the electrode. As shown in Figure 5-3(b) and Figure 5-3(c), three changes in appearance were observed after CV: a deformation of the glass, a color change from transparent to brown at the sides and bottom, and the formation of black reduction products.

Figure 5-3(d) shows the CV for simulant 1 measured for five consecutive cycles. A blank CV which was measured by using only a stainless-steel rod is also shown in thin black curve. The apparent current density was calculated from the area of stainless steel rod in contact with the molten salt. As with the behaviors of SiO₂ and Pyrex[®] glasses (in Chapter 3), the current increased

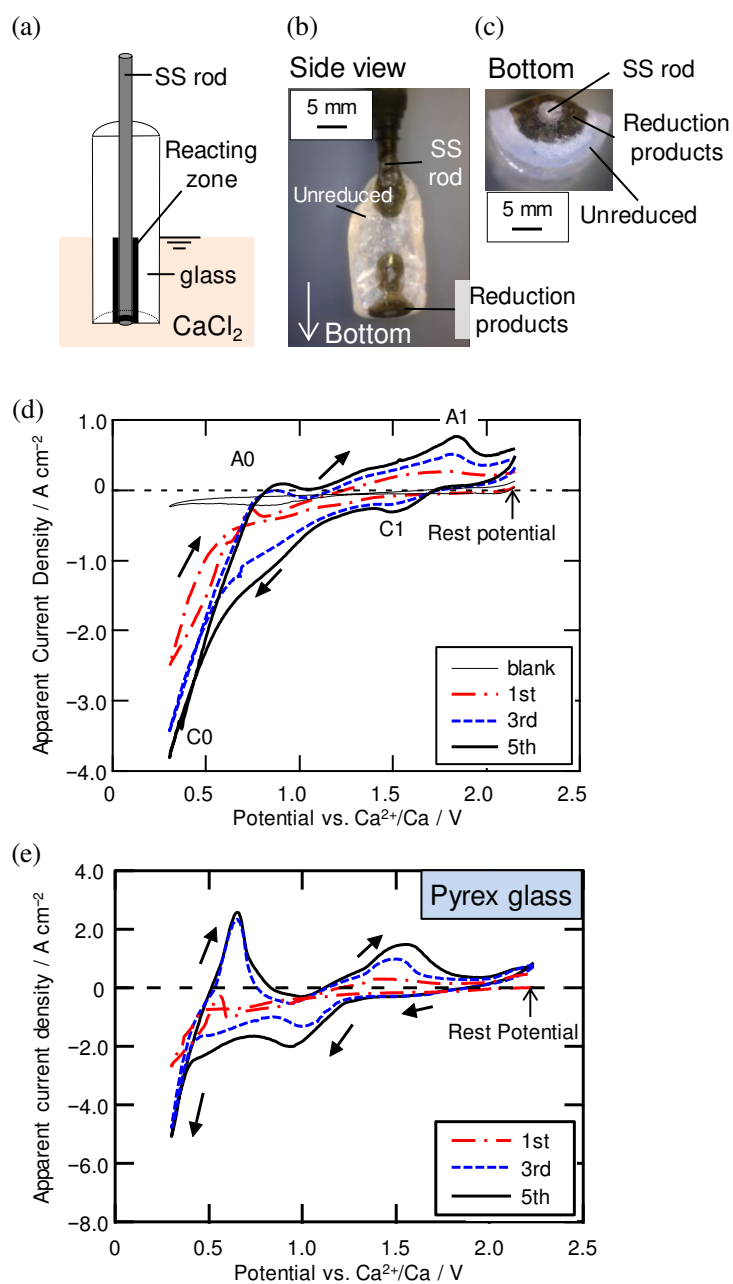


Figure 5-3 (a) Schematic of the vertical half of the glass-sealed electrode. (b) Side view and (c) bottom view of the glass-seal electrode after cyclic voltammetry (simulant 1). (d) Cyclic voltammograms of the glass-seal electrode of simulant 1 in the 1st, 3rd, and 5th cycles in molten CaCl_2 at 1103 K. Scan rate: 100 mV s^{-1} . (e) Cyclic voltammograms of the glass-seal electrode of Pyrex® glass in the 1st, 3rd, and 5th cycles in molten CaCl_2 at 1123 K. Scan rate: 100 mV s^{-1} .

with increasing cycle number because of the increase in the reaction zone.

The CV features of simulant 1 are similar to those for Pyrex[®] glass. For Pyrex[®] glass (shown in Figure 5-3(e)), cathodic currents for the reduction of B₂O₃ and SiO₂ and a sharp increase of the cathodic current for the formation of Si–Ca alloys were observed at 1.8, 1.3, and 0.5 V, respectively. In the CV of simulant 1 (shown in Figure 5-3(d)), a cathodic current C1 is observed at 1.5 V. The reduction of ZnO and B₂O₃ likely corresponds to the C1 considering the potential– pO^{2-} diagram for the Zn–Ca–O–Cl system shown in Figure 2-8(b) and that for the B–Ca–O–Cl system shown in Figure 2-4. A rise of cathodic current from 1.2 V is attributed to the reduction of SiO₂ [3]. A steep increase of cathodic current (C0) from 0.5 V is due to the formation of Si–Ca alloys [3]. After potential sweep is reversed, anodic current A0 is observed at 0.8 V, which corresponds to the dissolution of Ca from Si–Ca alloy. Then, the anodic current corresponding to the oxidation of Si is observed around 1.5 V. Anodic current A1 at 1.8 V is considered to be caused by the oxidation of B and Zn.

5.3.2 Characterization of electrolyzed simulant 1

The mixed powder of the simulant 1 and CaCl₂ was potentiostatically electrolyzed at 0.9 and 1.4 V.

Figure 5-4(a) shows a cross-sectional microscope image of the small crucible electrode electrolyzed at 1.4 V for 300 min. The sample was white, both before and after electrolysis. In the surface SEM image shown in Figure 5-4(b), two types of morphology can be seen: one is porous (point 1) and the other is flake-like (point 2). EDX analysis at point 1 clarifies that the porous parts are rich in SiO₂, and that the flake-like deposits have higher concentrations of Ca and Al compared to the original simulant 1. At both points, the concentration of Na is lower compared to that of the sample before electrolysis. Figure 5-4(c) shows an XRD pattern of the electrolyzed sample. The phase separation into α -quartz and anorthite (CaAl₂Si₂O₈) is confirmed, which is the same tendency as Pyrex[®] glass (in Chapter 3). Considering these results, the author concluded that the reduction

does not proceed significantly at 1.4 V, which is consistent with the fact that pure SiO₂ is not reduced at 1.4 V [4]. The formation of anorthite CaAl₂Si₂O₈ is explained by the ion exchange of Na⁺ in the glass with Ca²⁺ in the molten salt [5] and phase separation. In the ion exchange process at a temperature above the strain point, smaller ions are introduced to replace larger ones. The strain points of simulants 1 and 2 are around 773 K, which is below the temperature of the reaction with the molten salt. The strain point is defined as the temperature where the viscosity is 10^{14.5} dPa s [1]. Therefore, the Ca²⁺ ions replace Na⁺ ions (ion radius: Na⁺ > Ca²⁺). After ion exchange, the amount of CaO in the surface of the glass increases. Phase separation into SiO₂ and anorthite in the CaO–Al₂O₃–SiO₂ system has been reported previously the Ca²⁺ ions replace Na⁺ ions (ion radius: Na⁺ > Ca²⁺). After ion exchange, the amount of CaO in the surface of the glass increases. Phase separation into SiO₂ and anorthite in the CaO–Al₂O₃–SiO₂ system has been reported previously [6]. In that

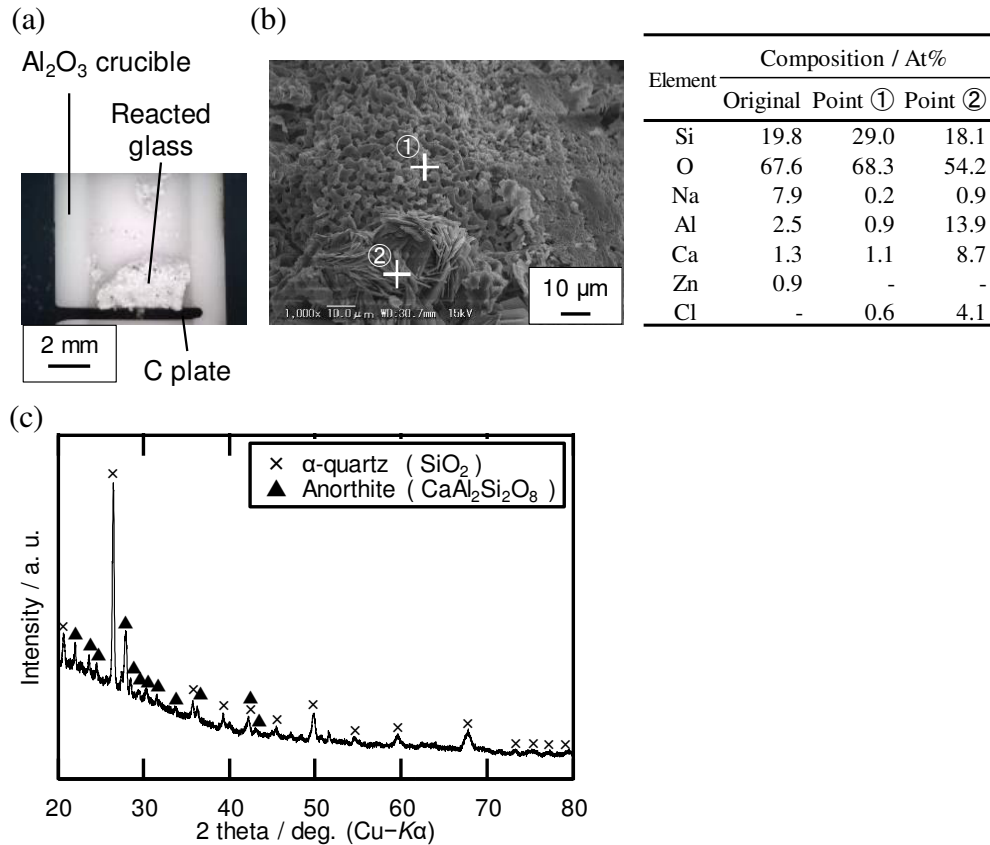


Figure 5-4 (a) A cross-sectional microscope image of the small crucible obtained by potentiostatic electrolysis of simulant 1 at 1.4 V for 300 min in molten CaCl₂ at 1103 K. (b) An SEM image, EDX analysis results, and (c) XRD pattern of the sample.

report, the crystallized glass was synthesized by the heat treatment of $(x-1)\text{SiO}_2-(100-x)\text{CaAl}_2\text{O}_4-1\text{Si}$ ($x = 70, 76, 80, 90$) with 0.3 mol% Eu_2O_3 at 1173 K for 12 h and at 1923 K for 3 h, and the phase separation into SiO_2 and anorthite was confirmed. Although the reduction of B_2O_3 and ZnO at 1.4 V is indicated by the potential- $p\text{O}^{2-}$ diagrams and CV, no XRD peaks for Zn and B compounds were observed. The reduction of B_2O_3 and ZnO proceeds only at the surface of the carbon plate and does not propagate to the bulk simulant because the main component, SiO_2 , is not reduced.

Figure 5-5(a) shows a cross-sectional microscope image of the small crucible electrode after electrolysis at 0.9 V for 300 min. The color of the reduction product is brown. In the SEM image in Figure 5-5(b), there are wires of sub-micron diameters. EDX point analysis indicates that simulant 1 is partly reduced to a Si-rich phase containing around 40 at% oxygen. Figure 5-5(c) shows an XRD pattern of the reduction product after washing with distilled water. The formation of Si is observed, in addition to calcium silicates (CaSiO_3 and $\text{Ca}_2\text{SiO}_3\text{Cl}_2$). In the potential- $p\text{O}^{2-}$ diagram for the Si-Ca-O-Cl system, CaSiO_3 is stable in the low $p\text{O}^{2-}$ region (shown in Figure 2-3(a)). The dissolution of alkali oxides, Na_2O and Li_2O , induces an increase in the concentration of O^{2-} ions and the formation of calcium silicates. After removing the calcium silicates from the reduction product by washing with an HCl solution, distinct peaks for Si, CaB_6 , and α -quartz appeared. Thus, the formation of Si and CaB_6 is confirmed in the potentiostatic electrolysis at 0.9 V. According to the potential- $p\text{O}^{2-}$ diagram for the B-Ca-O-Cl system (shown in Figure 2-4), the formation potential of CaB_6 (0.46 V) is more negative than the present electrolysis potential (0.9 V). Although the experimental result of CaB_6 formation disagrees with the thermodynamic data, the electrochemical formation of CaB_6 without the formation of elemental B in molten CaCl_2 -NaCl has been reported by Yin *et al.* [7].

From these results, the author concluded that the mixed powder of simulant 1 and CaCl_2 was electrochemically reduced, even though the softening point (863 K) is lower than the experimental temperature (1103 K).

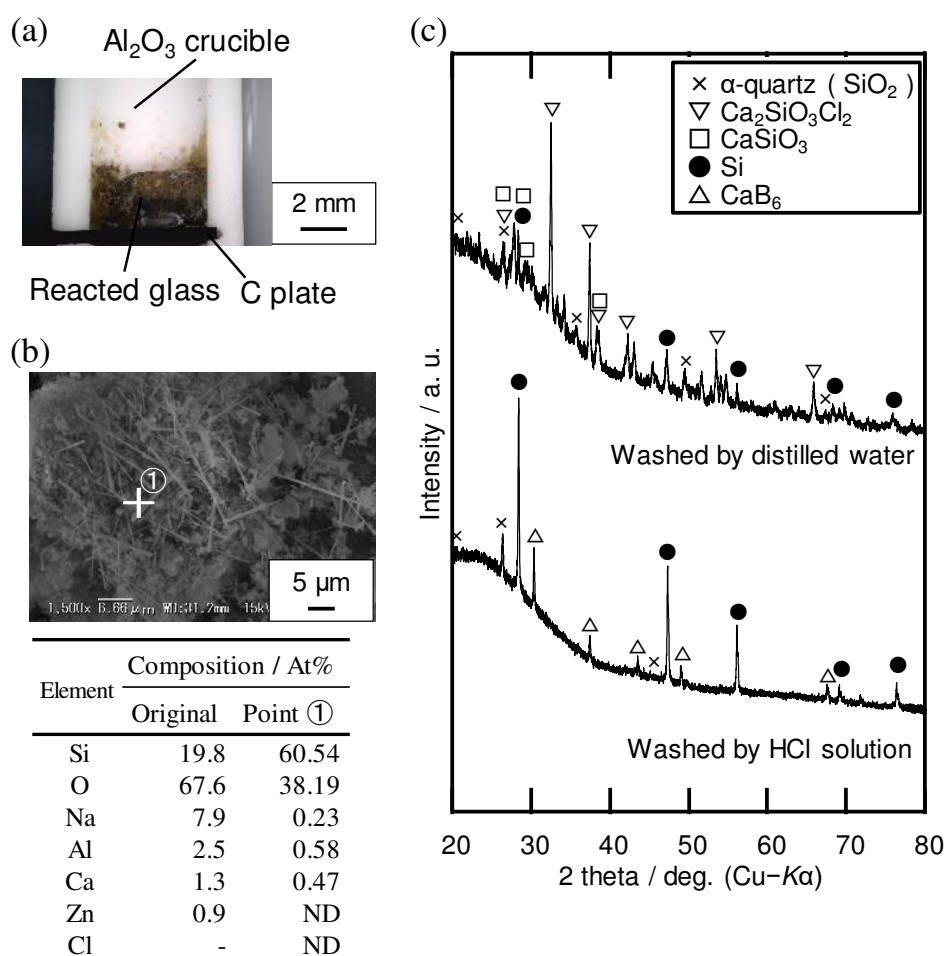


Figure 5-5 (a) A cross-sectional microscope image of the small crucible obtained by potentiostatic electrolysis of simulant 1 at 0.9 V for 300 min at 1103 K. (b) An SEM image, EDX analysis results, and (c) XRD patterns of the samples after washing with distilled water or HCl solution.

5.3.3 Characterization of the electrolyzed simulant 2

Based on the reduction method established in Section 5.3.2, the pellet prepared from the mixture of simulant 2 and the CaCl_2 powder was potentiostatically electrolyzed at different potentials and durations.

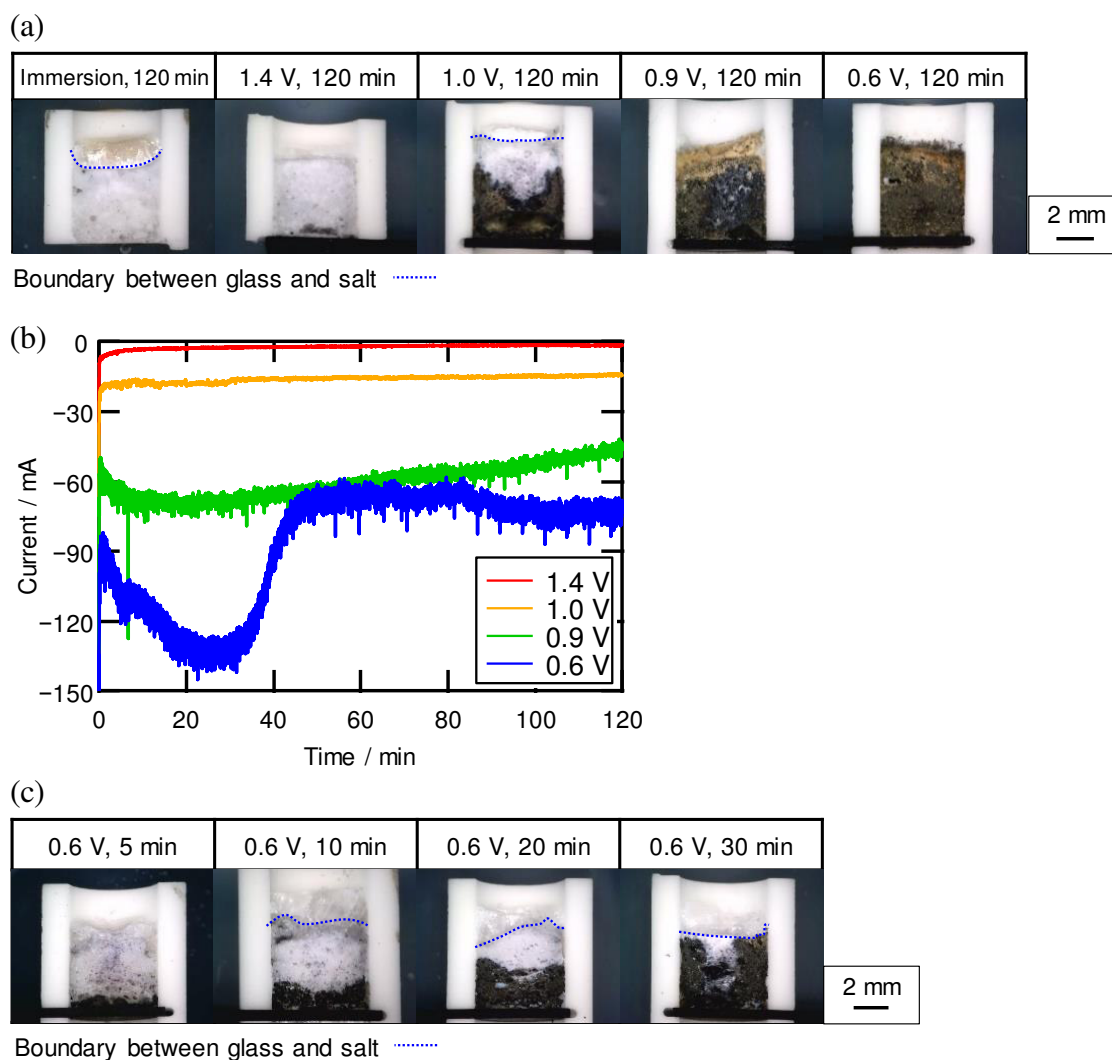


Figure 5-6 (a) Cross-sectional microscope images of the samples obtained by immersion and potentiostatic electrolysis of simulant 2 and (b) current-time curves during potentiostatic electrolysis at 1.4, 1.0, 0.9, and 0.6 V vs. Ca^{2+}/Ca for 120 min in molten CaCl_2 at 1103 K. (c) Cross-sectional microscope images of the samples obtained by potentiostatic electrolysis of simulant 2 at 0.6 V for 5, 10, 20, and 30 min.

For comparison, immersion samples were also prepared by immersing the mixture pellets into molten CaCl_2 for 120 min. The cross-sectional images of the immersed and reduced samples are shown in Figure 5-6(a). No color changes were observed in the samples after immersion and potentiostatic electrolysis at 1.4 V in the same manner as for simulant 1. On the other hand, half of the pellet had become brown at 1.0 V, indicating reduction. At 0.9 V, the upper part was pale brown and the lower part was brown. After electrolysis at 0.6 V, the overall

appearance of pellet had become brown. Figure 5-6(b) shows the current-time curves. Since almost constant currents were observed at 0.9, 1.0, and 1.4 V, the reduction may not have been completed by the end of electrolysis. At 0.6 V, the current rapidly decreased after 40 min, suggesting the complete reduction of the surface of the pellet. After 40 min, the constant current was observed. There are two possible contributions. One is the reduction reaction of unreduced oxides inside the sample. The overall appearance of the pellet is black, but the unreduced part may remain especially inside of the pellet where the diffusion path length of O^{2-} ions is long. Therefore, the reduction reaction current was still observed. The other contribution is the background current in the bath. After the reduction of glass, the conductive area on the surface of the reduction products increased. Therefore, a large background current was observed.

Figure 5-6(c) shows cross sections of the small crucible electrodes after electrolysis at 0.6 V for 5, 10, 20, and 30 min. The reduction layer grew with electrolysis time from the bottom conductor. The growth rate of the reduction layer at 0.6 V in the present study is approximately 1.5 times larger compared with the reduction of pure SiO_2 at 0.6 V in the study conducted by Yang *et al.* [8]. While $CaCl_2$ was not mixed to SiO_2 in ref. [8], $CaCl_2$ was mixed to simulant 2 at the weight ratio of $CaCl_2$ /simulant 2 of 0.4. Thus, the total volume was *ca.* 1.5 times larger than the actual volume of simulant 2. Then, the effective reduction speed of simulant 2, which is the reduction speed excluding the volume of $CaCl_2$, is almost the same as that of SiO_2 .

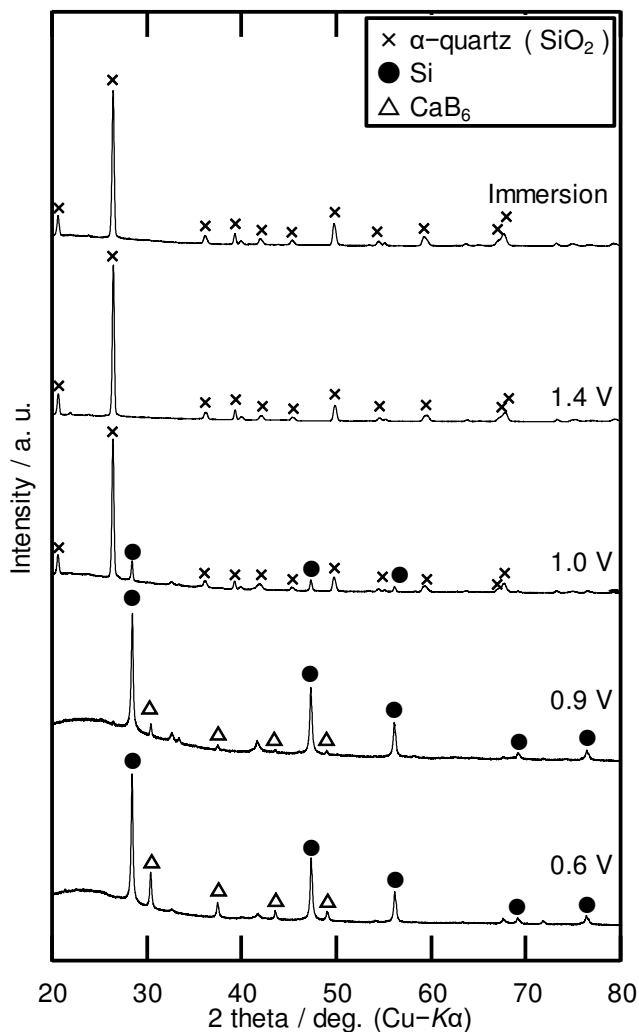


Figure 5-7 XRD patterns of the samples obtained by immersion and potentiostatic electrolysis of simulant 2 at 1.4, 1.0, 0.9, and 0.6 V vs. Ca^{2+}/Ca for 120 min in molten CaCl_2 at 1103 K, followed by washing with an HCl solution.

Figure 5-7 shows XRD patterns of simulant 2 samples obtained by immersion and electrolysis at 1.4, 1.0, 0.9, and 0.6 V for 120 min followed by washing with HCl solution. The XRD pattern of the immersion sample contains peaks assigned to α -quartz. Similar to the XRD pattern of simulant 1 (shown in Figure 5-5), the formation of α -quartz at 1.4 V was also confirmed. In the XRD pattern of the sample electrolyzed at 1.0 V, both α -quartz and Si were identified, which is consistent with the cross-sectional image in Figure 5-6(a). From the XRD patterns of the samples electrolyzed at 0.9 and 0.6 V, the components of simulant 2 are reduced to form Si and CaB_6 .

5.3.4 Behaviors of LLFP elements and the components in simulant 2

To clarify the distribution of elements after the electrolysis of simulant 2, the reduction products, remaining glass, and the molten salt were analyzed by ICP-AES/MS. Table 5-2 shows the results of ICP-AES/MS analysis for the solid samples after immersion and other samples obtained by the reduction at 0.6 V. The ICP-AES/MS results for the molten salt sampled after the series of experiments are listed in Table 5-3. The immersion and electrochemical reduction experiments were conducted in the same molten CaCl_2 . Thus, the dissolution ratio shown in Table 5-3 indicates the average value in various experimental conditions. The behaviors of the elements can be categorized into three types, as illustrated in Figure 5-8.

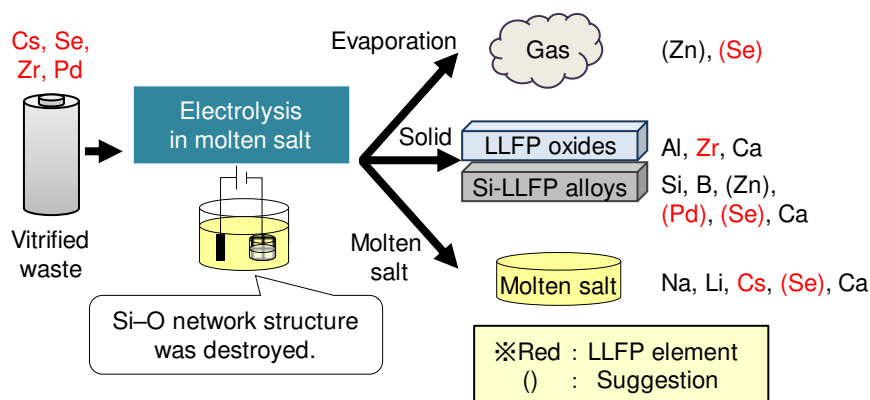


Figure 5-8 The behavior of the elements during the electrochemical reduction of simulant 2 in molten CaCl_2 .

Table 5-2 **Distribution of element in solid products for simulant 2 after immersion or reduction at 0.6 V in molten CaCl₂ at 1103 K. The concentration of element was analyzed by ICP-AES/MS.**

Element	Distribution of each element in solid products, α_{solid}^i (%)		
	Immersion, 180 min	0.6 V, 180 min, as reduced	0.6 V, >180 min, washing with HCl solution
Si	134.4	94.7	88.5
B	8.6	92.5	44.1
Na	0.0	1.1	0.0
Al	60.0	138.1	2.0
Li	0.0	3.4	0.0
Zn	0.8	50.0	5.1
Pd*	144.5	62.7	120.3
Zr (HF+HNO ₃)	111.2	40.0	63.3
Zr* (HCl+HNO ₃)*	35.0	35.1	35.0
Cs*	0.1	11.3	0.0
Se*	65.3	29.8	16.5

* Measured by ICP-MS

- : Not detected

Table 5-3 **Dissolution ratio of elements in molten salt for simulant 2 after the series of experiments. Totally *ca.* 2.6 g of simulant 2 was used. For reference, calculated maximum concentrations ($\alpha_{\text{dis}}^i=100$ %) of elements (ppmw) in the molten salt after the series of experiments and impurity concentrations of elements in CaCl_2 used in this study (ppmw) are also listed. All the concentrations of elements were analyzed by ICP-AES/MS.**

Element	Dissolution ratio for molten salt, α_{dis}^i (%)	Calculated maximum concentrations ($\alpha_{\text{dis}}^i=100$ %) of elements (ppmw) in the molten salt after the series of experiments	Impurity concentrations of elements in CaCl_2 used in this study (ppmw)
Si	8.4	1650	< 32
B	21.5	329	< 3.0
Na	114.8	389	< 96*
Al	2.0	124	3.05*
Li	103.6	85.7	0.938*
Zn	0.1	189	0.436*
Pd*	0.3	12.1*	< 0.03*
Zr*	2.1	64.5*	0.29*
Cs*	85.4	32.5*	0.007*
Se*	7.5	1.7*	< 0.02*

* Measured by ICP-MS

Group 1: Dissolution into the molten salt

Na, Li, and Cs primarily dissolve into the CaCl_2 molten salt, which is consistent with the thermodynamic prediction (Figure 2-7(a), 2-8(a), and 2-9(b)). In particular, for Na and Li, the dissolution ratio was almost 100%. For Cs, which is one of the LLFPs, more than 80% is dissolved into the molten salt, but 10% remained in the sample. The dissolution of Cs_2O is considered to be slower than those of Li_2O and Na_2O .

Group 2: Remaining in the solid phase

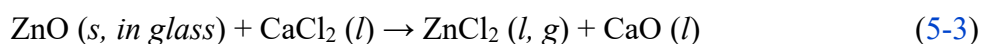
Most of Si remains in the solid products for both the immersion products and reduction products. The SiO_2 is reduced to Si at 0.6 V, which is also reasonable in the potential- $p\text{O}^{2-}$ diagram for the Si–Ca–O–Cl system. A small amount of Si (8.4%) dissolves into the molten salt. With the dissolution of Na_2O , Li_2O , and Cs_2O , the number of O^{2-} ions increase and SiO_2 is thought to dissolve in the form of silicate (SiO_3^{2-}) ions.

While B comprises less than 10% of the solid product after immersion, most of the B (94.7%) remains in the solid product after electrolysis. B_2O_3 is considered to be dissolved into molten salt because of the increase in O^{2-} ions, thus forming borate ($\text{B}_2\text{O}_4^{2-}$) ions. With electrolysis, boron remains as Si–B alloys (in Chapter 3) and CaB_6 in the solid.

Al, Zr (LLFP), and Pd (LLFP) remain in the solid products and do not dissolve into the molten salt. Several stable compounds such as calcium aluminate, calcium zirconate, ZrO_2 , and their metals remain in the solid phase depending on the $p\text{O}^{2-}$ value and potential. After washing with HCl solution, the amount of Al in the solid phase decreased to 2%, and the Al compounds in the solid products could have reacted with the HCl solution, thereafter being removed. Here, CaSiO_3 , CaB_4O_7 , a part of calcium aluminates, Al, ZnO, and Zn are expected to be removed by HCl solution. From the results, ZnO and elemental Zn have been actually removed by washing with HCl solution.

Group 3: Dissipation from the system

For Zn, the behavior is different between immersion and electrolysis. After immersion in CaCl_2 , the Zn compounds did not remain in either the solid phase or the molten salt. The behavior can be explained by evaporation. From the potential– $p\text{O}^{2-}$ diagram for the Zn–Ca–O–Cl system (Figure 2-8(b)), ZnO in the simulant glass is suggested to react with molten CaCl_2 to form $\text{ZnCl}_2(\text{g})$ above 1.84 V vs. Ca^{2+}/Ca in the range $p\text{O}^{2-} > 4.32$.



The formed $\text{ZnCl}_2(\text{l})$ in the melt is gradually evaporated from the molten salt because of its high vapor pressure at 1103 K. On the other hand, Zn remains in the solid product after the reduction, and, probably, ZnO was reduced to Zn alloy phases.

The behavior of Se (LLFP) is also different between immersion and electrolysis. When the simulant glass is immersed in CaCl_2 without electrolysis, more than 60% of the Se compounds remain in the solid part despite thermodynamic prediction. One of the reasons for the discrepancy is the small activity of selenium oxides in the glass. The glass network structure can prevent the evaporation of selenium component when the glass was immersed. After electrolysis at 0.6 V, the amount of Se in the solid part decreased to 30%, and the amount of Se detected in the molten salt was less than 10%. Se is suggested to partially evaporate as elemental gas ($\text{Se}_2(\text{g})$), oxides, and chloride and partially in the solid phase as solid selenium compounds such as $\text{CaSe}(\text{s})$ during electrolysis of the simulant glass. It agrees with the potential– $p\text{O}^{2-}$ diagram for Se–Ca–O–Cl. From the value of the analysis of molten salt, some of selenium compounds such as $\text{CaSe}(\text{s})$ may be dissolved into molten salt as ions.

5.4 Conclusion

The electrochemical reduction behavior of simulant 1 (glass component only) and simulant 2 (also containing LLFPs; Zr, Cs, Pd, and Se) was investigated in molten CaCl_2 at 1103 K. For simulant 1, phase separation and the dissolution of Na_2O were confirmed at 1.4 V (vs. Ca^{2+}/Ca). The reduction of the simulant glass with a lower-softening point than the experimental temperature was achieved by mixing the glass with CaCl_2 in advance. The reduction reactions of SiO_2 to Si and B_2O_3 to CaB_6 were confirmed at 0.9 V. For simulant 2, the behavior of the LLFPs and other elements were investigated by the analysis of the solid products after immersion and reduction in molten CaCl_2 , as well as the analysis of the molten salt sampled after the experiments. Na_2O , Li_2O , and Cs_2O were dissolved into the molten salt. On the other hand, Al, Zr, and Pd remained in the solid part. Si, B, and Se were partially dissolved in the molten salt. Although a large part of the Se remained in the solid part after the immersion, its concentration decreased after electrolysis. Finally, although Zn compounds were evaporated in the case of immersion, they remained in the solid after electrolysis. Through this study, the behaviors of LLFP elements during the electrolysis of vitrified waste simulants were almost clarified. In the future, it is necessary to develop the subsequent recovery processes such as a recovery of Cs from the molten salt by electrolysis. Also, experiments on the simulant which has the same composition of vitrified radioactive waste are necessary.

5.5 Reference list

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Chapter 6

Electrochemical reduction of vitrified waste simulants

6.1 Introduction

In previous chapters, the electrochemical reductions of borosilicate glass and two types of simplified simulants of vitrified radioactive waste have been investigated. Their compositions are listed in [Table 1-5](#). In the electrochemical reduction of borosilicate glass, the main component, SiO_2 , was reduced to crystalline Si by potentiostatic electrolysis at 0.9 V vs. Ca^{2+}/Ca in molten CaCl_2 at 1123 K (in Chapter 3). The reduction of B_2O_3 and the dissolution of Na_2O were also indicated (in Chapter 3). The behaviors of the constituent elements, i.e., Si, B, Al, Na, and K, agreed with the potential– $p\text{O}^{2-}$ diagrams constructed from the thermodynamic data (in Chapter 2 and 3). In the subsequent study, the electrochemical reduction of two types of simplified simulants of vitrified radioactive waste, simulant 1 (glass component only: SiO_2 , B_2O_3 , Na_2O , Al_2O_3 , CaO , Li_2O , and ZnO) and simulant 2 (also containing long-lived fission product oxides, ZrO_2 , Cs_2O , PdO , and SeO_2), was investigated in molten CaCl_2 at 1103 K (in Chapter 5). The dissolution of Na, Li, and Cs from the simulants into molten CaCl_2 was confirmed. Most of the SiO_2 in the simulants had been reduced to Si after the electrolysis at 0.9 V vs. Ca^{2+}/Ca . After the electrolysis of simulant 2, Al, Zr, and Pd remained in the solid phase. SeO_2 was found to remain partially in the solid phase and partially evaporate.

In the present chapter, the glass with almost the same composition to the real vitrified waste was prepared, which is hereafter referred as simulant 3. The approximate composition of simulant 3 is listed in [Table 1-5](#). Simulant 3 is composed of 33 oxides and its detailed composition

is listed in [Table 1-6](#). Here, simulant 3 was prepared by using only stable isotopes and replacing uranium with cerium to avoid radioactivity. Before the experiment, potential- pO^{2-} diagrams were constructed to predict the behaviors of constituent elements during the electrochemical reduction (in Chapter 2). Then, the following two experiments were conducted: Simulant 3 was electrochemically reduced in molten $CaCl_2$ with the small crucible electrode in experiment 1 and with the large crucible electrode in experiment 2. The reduction products were analyzed by field emission scanning electron microscope (FE-SEM), XRD, and ICP-AES and -MS. Sampled molten salts were also analyzed by ICP-AES and -MS.

6.2 Experimental

6.2.1 Experiment 1 (Small crucible)

Experimental setup and procedure is the same as in Chapter 5. 450 g of $CaCl_2$ (> 99 %, Kojundo Chemical Laboratory Co., Ltd.) was prepared. Electrochemical measurements and potentiostatic electrolysis were conducted with a three-electrode method using an electrochemical measurement system. The counter electrode and reference electrode were the same as in Chapter 3. For electrochemical measurements, a glass-seal electrode was prepared for a working electrode in the same method as simulant 1 in Chapter 5.

For potentiostatic electrolysis, a small crucible electrode shown in [Figure 5-1\(b\)\(c\)](#) in Chapter 5 was used. In the electrolysis of simulant 3, a pellet (dia. 5 mm) was prepared from the mixed powder of simulant 3 and $CaCl_2$ (< 0.212 mm) in the open dry chamber. The ratio of simulant and $CaCl_2$ was 1:0.4 by weight, and the weight of simulant used was around 100 mg. A pellet was prepared under around 0.3 MPa, and was transferred into the small crucible electrode. The Ni lead wire of the small crucible electrode was finally spot-welded to a Mo wire of the electrode.

After potentiostatic electrolysis, the samples were taken out from the molten salt and rinsed with distilled water to remove the residual salts. After removing the Ni wires, the samples were cut by the desktop abrasive cutting machine. The cross-section was observed by using an

optical digital microscope. After the observation, the samples were firstly soaked in 8 wt% HCl solution for longer than 8 hours to remove the salt and calcium silicates adhered to the samples. Then, the remaining solid was recovered from the solution by suction filtration, dried at 353 K, and analyzed by XRD. The samples were also observed by FE-SEM (JSM-6500FE, JEOL Co., Ltd.),

For ICP-AES and MS analysis, the samples were not cut after the potentiostatic electrolysis. The residual salt was dissolved by distilled water, and Ni wires were removed. Two different methods were adopted for analysis. In the first method, the samples were stirred in 3 M HCl solution by a magnetic stirrer for 48 hours. The solid and liquid phases were separated by suction filtration. The solid phase was dissolved into the mixture solution of 2.35 mL of 38 wt% HF and 3.28 mL of 68 wt% HNO₃ for 24 hours. The HF+HNO₃ solution was recovered by suction filtration, and then ultrapure water was added to be a total volume of 100 mL. Both HCl and HF+HNO₃ solutions were analyzed by ICP-AES and ICP-MS. In the second method, samples were dissolved into HNO₃+HCl+HF (1:1:1, volume ratio) solution by using microwave decomposition machine (ETHOS One, Milestone Co., Ltd) at 503 K. The solution was analyzed by ICP-AES and MS.

For the composition analysis, molten salts were sampled by the suction method using a mullite tube (o.d.: 5 mm, i.d.: 3 mm, Nikkato Corp.) and a pipet bulb. The solidified salt collected in the tube was weighed in the open dry chamber. Approximately 3 g of the collected salt was dissolved in 100 mL of 1 M HNO₃ solution and analyzed by ICP-AES and MS.

6.2.2 Experiment 2 (Large crucible)

Figure 6-1 shows a schematic of the experimental apparatus for experiment 2. The weight ratio of CaCl₂ to glass was *ca.* 20. First, 200 g of CaCl₂ (> 99 %, Kojundo Chemical Laboratory Co., Ltd.) were put in a graphite crucible (i.d. 80 mm, height 150 mm, Toyo Tanso Co., Ltd.) in the open dry chamber. A graphite rod was connected to the crucible with carbon bolts and nuts. The experiment was conducted inside the quartz glass vessel at 1103 K in a dry Ar atmosphere.

Dozens of pellets were fabricated in the same manner with Exp. 1. Total weights of simulant 3 and CaCl_2 in the pellets were *ca.* 10 g and *ca.* 4 g, respectively. After raising up the temperature, all the pellets were put into the melts.

Galvanotactic electrolysis was conducted with a three-electrode method using an electrochemical measurement system (HZ-7000, Hokuto Denko Corp.). The counter electrode and reference electrode were the same as Exp. 1. For the composition analysis, molten salts before and after the electrolysis were measured by ICP-AES and -MS. In Exp. 2, the amounts of initial impurities were subtracted in the evaluation. The reduction products were collected after removing CaCl_2 by distilled water at 353 K on a hot plate. After suction filtration and drying at the room temperature, the collected products were weighted. A part of the collected products was rinsed in HCl solution and dried on the hot plate before XRD analysis. The other parts of the products were analyzed by three different methods. In the main method, microwave dissolution was conducted for two times: The sample was dissolved into HNO_3+HCl (1:3, volume ratio) solution at 503 K with microwave dissolution, and the recovered solid phase by filtrations was further dissolved into $\text{HNO}_3+\text{HCl}+\text{HF}$ (1:1:1, volume ratio) at 503 K with microwave dissolution. The other two methods were the same as in Exp. 1. These solutions were analyzed by ICP-AES and -MS. The distributions of the constituent elements were calculated from the weight of analyzed sample and the results of the ICP-AES and -MS. Among the three different dissolution methods, the method that gave the closest value to unity for the sum of distribution ratios in the solid reduced product and the molten salt was chosen for each element.

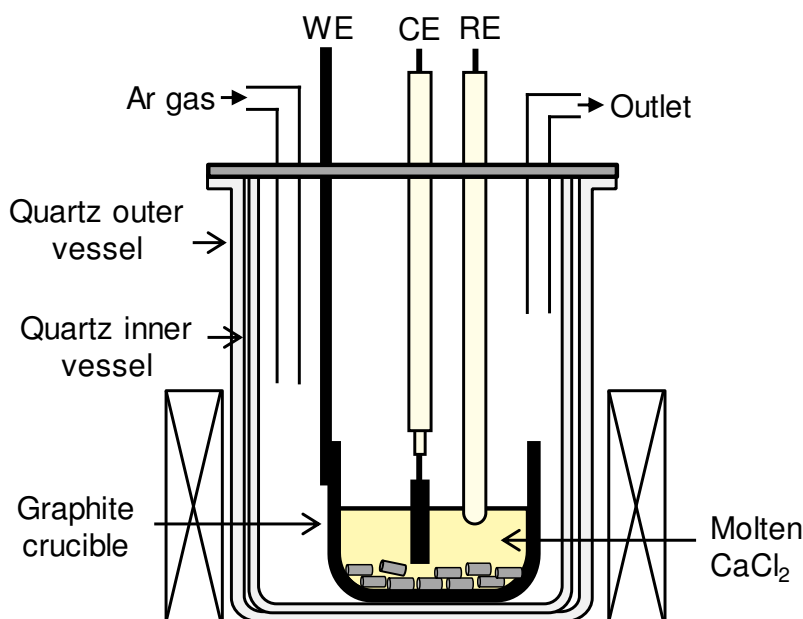


Figure 6-1 Schematic figure of the experimental apparatus for electrochemical reduction of a large amount of simulant 3. (Exp. 2)

6.3 Results and discussion

6.3.1 Cyclic voltammetry

Figure 6-2(a) shows a schematic of the vertically cut section of the glass-seal electrode using simulant 3. A small amount of the glass was used to prevent the disappearance of the three-phase interface during the measurement due to the softening of the glass. The reaction zone locates at the three-phase interface between glass, the stainless steel rod, and molten CaCl_2 both at the side and bottom of the electrode, which is shown in red in Figure 6-2(a). Figure 6-2(b) and (c) show the photographs of the electrode before and after the cyclic voltammetry. In the same behavior with simulant 1 whose composition is shown in Table 1-5, three changes in the appearance were observed after cyclic voltammetry: a deformation of the glass, the color change from no-color to brown at the side and bottom, and the formation of black-colored reduction products.

Figure 6-2(d) the cyclic voltammograms for five consecutive cycles measured by the glass-sealed electrode of simulant 3. The apparent current density is calculated from the area of stainless steel rod in contact with the molten salt. As well as the behaviors of SiO_2 and Pyrex[®]

glasses (in Chapter 3) and simulant 1 (in Chapter 5), the current increases with the cycle number due to the increase of reaction zone.

The shape of the voltammogram is similar to that for simulant 1 even though simulant 3 contains many kinds of metal oxides which were not included in simulant 1. In the previous study for simulant 1 (in Chapter 5), cathodic currents for the reduction of $\text{B}_2\text{O}_3 + \text{ZnO}$ and SiO_2 were observed at 1.8 V and 1.3 V, respectively. In addition, sharp increase of cathodic current for the formation of Si–Ca alloys was seen at 0.5 V. In the present study for simulant 3, the cathodic current at 1.8 V will also correspond to the reduction of oxides, whose $\Delta G_f^\circ (\text{MO}_x)$ is negatively larger than $\Delta G_f^\circ (\text{SiO}_2)$, such as MO_x ($\text{M} = \text{Mn, Cr, P, B, Zn, etc.}$). The cathodic current from 1.3 V to 0.3 V will correspond to the reductions of SiO_2 and the oxides more stable than SiO_2 such as MO_x ($\text{M} = \text{Al, Zr, Eu, Nd, etc.}$). Here, the cathodic current at 0.3–0.4 V also includes the formation reaction of Si–Ca alloy. After reversing the scan direction at 0.3 V, the current for the dissolution of Ca from the formed Si–Ca alloy is observed at 0.5–0.8 V. The anodic current observed from 1.0 V will correspond to the oxidations of the Si and other metals.

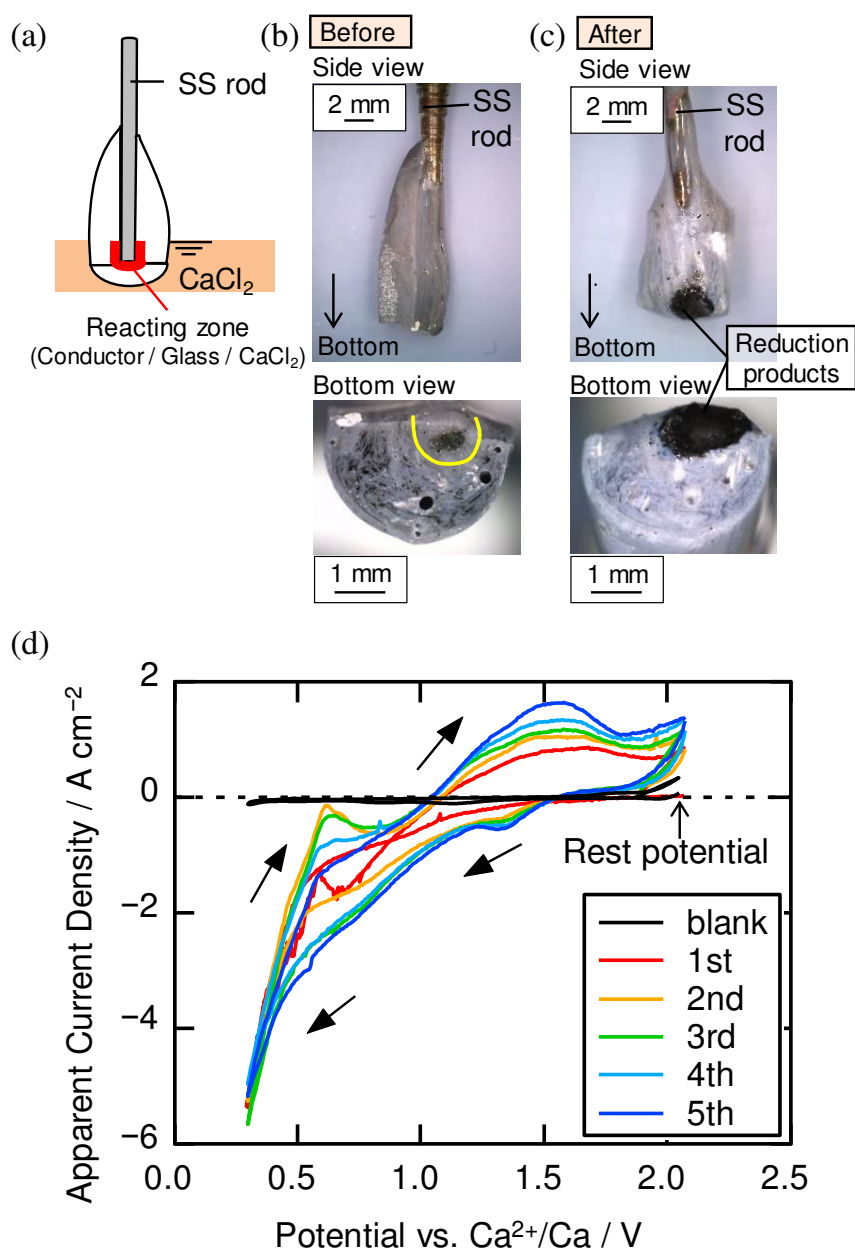


Figure 6-2 (a) Schematic of the vertical half of the simulant glass-sealed electrode. Side view and bottom views of the glass-sealed electrode (b) before and (c) after cyclic voltammetry. (d) Cyclic voltammograms for the glass-sealed electrode from 1st to 5th cycles in molten CaCl_2 at 1103 K. Scan rate: 100 mV s^{-1}

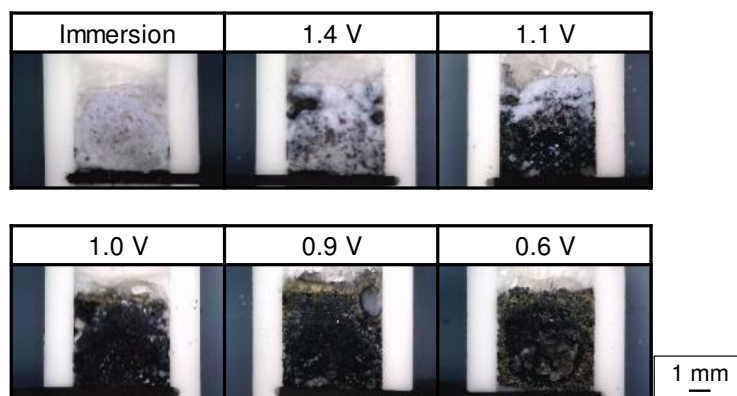
6.3.2 Analysis of the electrolyzed simulant 3 in Exp. 1

The pellet prepared from the mixture of simulant 3 and CaCl_2 powder was potentiostatically electrolyzed at different potentials and duration times. Figure 6-3(a) shows cross-sectional microscope images of the small crucible electrodes immersed and electrolyzed at 1.4, 1.1,

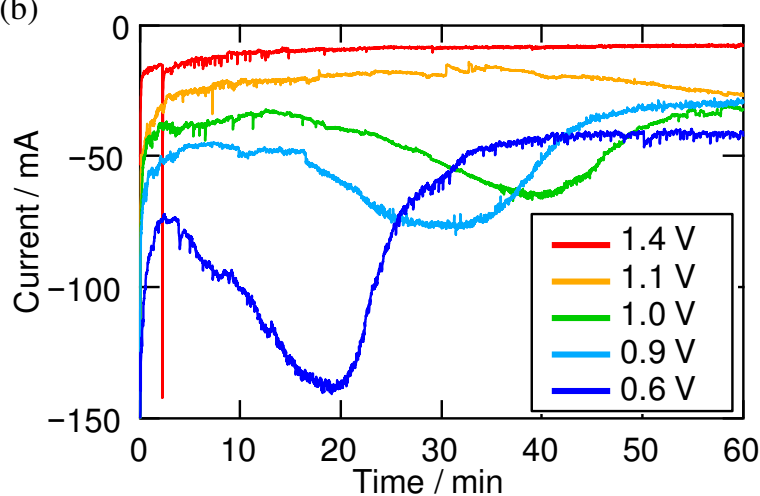
1.0, 0.9, and 0.6 V for 60 min. No color change was observed in the sample after immersion. At 1.4 V, the color of a part of the pellet became brown. This color change to brown, indicating reduction, was observed for half of the pellet at 1.1 V, while the whole pellet electrolyzed at 1.0, 0.9, and 0.6 V. In the current-time curves, as shown in Figure 6-3(b), almost constant currents were observed at 1.4 V and 1.1 V, suggesting the occurrence of incomplete reductions even at the end of the electrolysis process. At 1.0, 0.9, and 0.6 V, the current generally decreases after the peaks at 20–40 min. The current at 0.6 V rapidly decreases to around -50 mA after 30 min, suggesting the completion of the reduction of the whole pellet.

Figure 6-3(c) shows the cross-sections of the small crucible electrodes after electrolysis at 0.6 V for 5, 10, 20, and 30 min. Reduction layer growth increased from the bottom conductor as electrolysis time increased. The effective reduction speed was almost twice as high as that of simulant 2 (in Chapter 5). In this paper, effective reduction speed means the reduction speed excluding the volume of CaCl_2 . Some elements existing in their metallic states in the glass, such as platinum-group metals, might contribute to the acceleration of the reduction reaction.

(a) 60 min



(b)



(c) 0.6 V

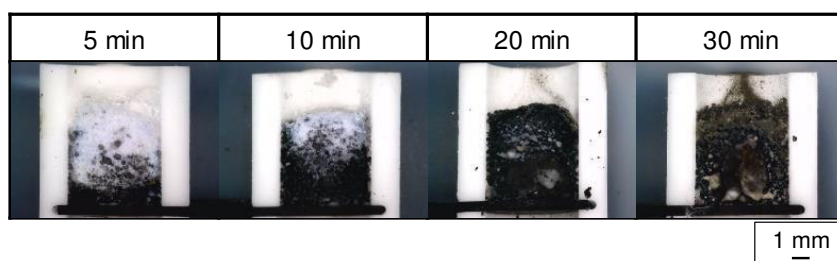


Figure 6-3

(a) Cross-sectional microscope images of the samples obtained by immersion and potentiostatic electrolysis of the simulant 3 and (b) current-time curves during potentiostatic electrolysis at several potentials for 60 min in molten CaCl_2 at 1103 K. (c) Cross-sectional microscope images of the samples obtained by potentiostatic electrolysis of the simulant 3 at 0.6 V for several duration time.

Figure 6-4(a) shows the XRD patterns of simulant 3 samples after being washed with the HCl solution. The immersion sample and the reduced samples at 1.4, 1.1, and 1.0 V have peaks assigned to α -quartz in the same manner as simulants 1 and 2 samples (in Chapter 5). The formation of a ruthenium palladium alloy ($\text{Ru}_{0.973}\text{Pd}_{0.027}$) was confirmed at 1.4 and 1.1 V. In the XRD pattern, at 1.1, 1.0, 0.9, and 0.6 V, the patterns attributed to Si, Ru_2Si_3 , and XB_6 were confirmed, where X = Ca or rare earth elements (REEs). The reduction of the main component of SiO_2 to Si is consistent with the color change observed in the cross-sectional images shown in Figure 6-3(a). Due to the similarity of the peak patterns for XB_6 (X = Ca or REE) owing to the same structure (Figure 6-4(b) and (c)), the compound was not identified. In the reduction products of simulant 1 (in Chapter 5), the formation of CaB_6 and SiB_6 likely occurred, according to the results. Furthermore, the formation of Si–B components in the reduction products of borosilicate glass was confirmed by X-ray photoelectron spectroscopy and Raman spectroscopy (in Chapter 3). The relatively strong peak observed at $2\theta = 21.4^\circ$ for the samples at 0.9 V and 0.6 V indicates that the reduction products contained XB_6 (X = REE), including CaB_6 and SiB_6 .

The formation of these compounds can be explained using the potential– $p\text{O}^{2-}$ diagrams. The formation of Ru–Pd alloys at positive potentials, such as 1.4 and 1.1 V, is reasonable because of the large stable region of elemental Ru and Pd in the potential– $p\text{O}^{2-}$ diagrams for the Pd–Ca–O–Cl system (in Chapter 2, Figure 2-9(c)) and the Ru–Ca–O–Cl system shown in Figure 2-13(a). As for REEs, the reduction potentials of these oxides, E° (X^{3+}/X vs. Ca^{2+}/Ca), i.e., the three-phase boundaries between elemental REEs (Y, La, Ce, Pr, Nd, and Gd) and chlorides, are 0.69, 0.49, 0.55, 0.53, 0.57, and 0.68 V, respectively, as seen in the potential– $p\text{O}^{2-}$ diagrams shown in Figure 2-12. The discrepancy between experimental results and thermodynamic data for the formation of CaB_6 has already been reported after the electrochemical reduction of simulant 1 (in Chapter 5) and CaB_2O_4 [1].

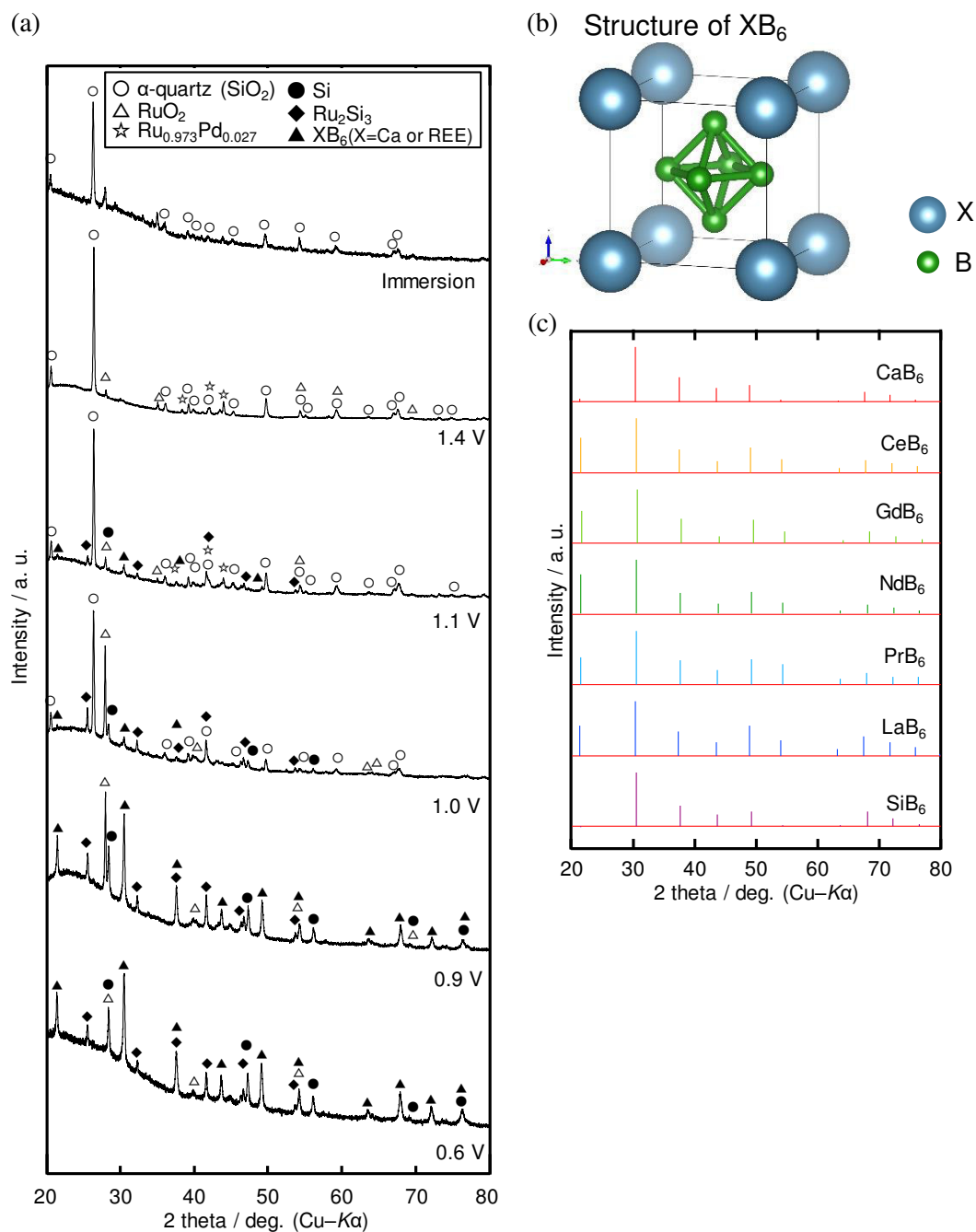


Figure 6-4 (a) XRD patterns of the samples obtained by immersion and potentiostatic electrolysis of the simulant 3 at several potentials for 60 min in molten CaCl_2 at 1103 K, followed by washing with HCl solution. (b) Structure of XB_6 ($\text{X} = \text{Ca or REE}$). (c) XRD patterns of standard sample of XB_6 ($\text{X} = \text{Ca, La, La}_{0.1}\text{Sm}_{0.9}, \text{Pr, and Si}$).

The formation of XB_6 was thermodynamically analyzed. Because the reduction of B_2O_3 to B occurs at positive potentials (even 1.1 V) and $p\text{O}^{2-} > 3.52$, the formation of XB_6 ($\text{X}=\text{REE}$) can be explained in the reaction presented in Equation 6-1. In this reaction, the potential for the reduction of oxides is equal to that for X^{3+} ions at the three-phase boundary between metal/oxide/chloride.



Since XB_6 and elemental B equilibrate according to the phase diagrams, the standard Gibbs energy of formation of XB_6 , $\Delta G_f^\circ(\text{XB}_6)$, was calculated from the standard formation potentials of XB_6 , $E^\circ(\text{X}^{3+}, \text{B}/\text{XB}_6 \text{ vs. } \text{X}^{3+}/\text{X})$.

$$E^\circ(\text{X}^{3+}, \text{B}/\text{XB}_6 \text{ vs. } \text{X}^{3+}/\text{X}) = -\frac{\Delta G_f^\circ(\text{XB}_6)}{3F} \quad (6-2)$$

Then, the formation potential of XB_6 with respect to the Ca^{2+}/Ca potential, $E^\circ(\text{X}^{3+}, \text{B}/\text{XB}_6 \text{ vs. } \text{Ca}^{2+}/\text{Ca})$, was obtained from the standard redox potential of X^{3+}/X .

$$E^\circ(\text{X}^{3+}, \text{B}/\text{XB}_6 \text{ vs. } \text{Ca}^{2+}/\text{Ca}) = E^\circ(\text{X}^{3+}, \text{B}/\text{XB}_6 \text{ vs. } \text{X}^{3+}/\text{X}) + E^\circ(\text{X}^{3+}/\text{X} \text{ vs. } \text{Ca}^{2+}/\text{Ca}) \quad (6-3)$$

Table 6-1 summarizes the author's evaluation of the formation potential of XB_6 based on the above discussion. While the standard Gibbs energy of formation of XB_6 ($\text{X} = \text{Ce}, \text{Gd}, \text{Nd}, \text{and La}$) at 1123 K [2–5] have been reported, thermodynamic data for PrB_6 and YB_6 are not available. In addition, the evaluation of the deposition of $\text{Sm}(s)$ is difficult in the proposed system (as shown in Figure 2-13(f)). As shown in the table, reduction products for potentials more positive than 1.1 V vs. Ca^{2+}/Ca are suggested, such as CeB_6 , GdB_6 , and NdB_6 .

Table 6-1 Standard Gibbs energy of formation and redox potential of X^{3+} , B / XB_6 (X = Ce, Gd, Nd, and La).

X	Ce	Gd	Nd	La
$\Delta G^\circ_f (XB_6)$ / kJmol^{-1}	-314.7	-126.7	-160.1	-81.20
Reference	[2,3]	[4]	[5]	[2,5]
$E^\circ (X^{3+}, B/XB_6)$ / V vs. X^{3+}/X	1.09	0.44	0.55	0.28
$E^\circ (X^{3+}/X)$ / V vs. Ca^{2+}/Ca	0.55	0.68	0.57	0.49
$E^\circ (X^{3+}, B/XB_6)$ / V vs. Ca^{2+}/Ca	1.63	1.11	1.12	0.77

Simulant 3 reduced at 0.6 V for 60 min was observed via FE-SEM after washing it with the HCl solution. As shown in Figure 6-5, a nanowire structure with a diameter of 300 nm was observed, especially at the upper side of the pellet. The morphology of the reduced sample was the same as that of previous reports on the electrochemical reduction of SiO_2 in molten CaCl_2 [6–8]. EDX analysis of the nanowire showed 67 at% Si, 22 at% O, 2 at% Ca, 5 at% Cl, and 2 at% Na. These results suggest that the reduction products contained calcium silicates. The formation of calcium silicates by electrochemical reduction of glass containing Na_2O agrees with previous research and thermodynamics calculations (in Chapter 2 and 3).

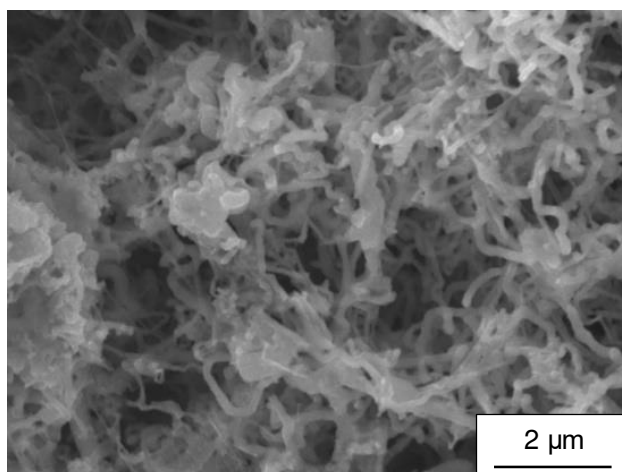


Figure 6-5 An FE-SEM image of reduced simulant 3 obtained by potentiostatic electrolysis of the simulated glass at 0.6 V for 60 minutes at 1103 K and washing by HCl solution.

6.3.3 Analysis of the electrolyzed simulant 3 in Exp. 2

Mass-scale electrochemical reduction is important to be able to industrialize the proposed process. For the reduction of a large amount of simulant 3, the author opted for a galvanostatic electrolysis process to prevent large currents at the initial stage of the electrolysis. The potential curve used during electrolysis at -2 A for 300 min is shown in [Figure 6-6\(a\)](#). The potential was gradually and negatively changed from 1.0 V to around 0.5 V. The total electric charge 36000 C corresponds to 114% of the theoretical quantity for the reduction of only the SiO_2 components in simulant 3.

[Figure 6-6\(b\)](#) shows a photograph of the reduction products obtained in the electrolysis of 9.77 g of simulant 3. Sample (A) shows a black powder, weighing 16.24 g, and (B) shows a mixture of unreduced pellets and reduced powder, weighing 6.00 g. These increased weights are in disagreement with the expectation that weight decreases by the reduction of oxides, i.e., by the removal of oxygen. The formation of CaSiO_3 , and CaB_6 would be the main reason for the increases of weight measured.

The reduction products in Sample (A) were characterized by XRD after washing them with the HCl solution. The reason for the difference between the reduction products in Exp. 1 and

2 (Figure 6-4(a)) might be the different composition of the melt. In Exp. 2, the ratio of simulant 3 to CaCl_2 was higher than in Exp. 1. The high concentration of O^{2-} ions in the melt in Exp. 2 were deduced from the electrochemical reduction behavior of Pyrex[®] glass and simulant 1 (in Chapter 3 and 5), and from the thermodynamics discussion accompanying (in Chapter 2). Due to the low $p\text{O}^{2-}$ value, the reduction of some REEs (Y, La, Ce, Pr, Nd, and Gd) did not occur in Exp. 2.

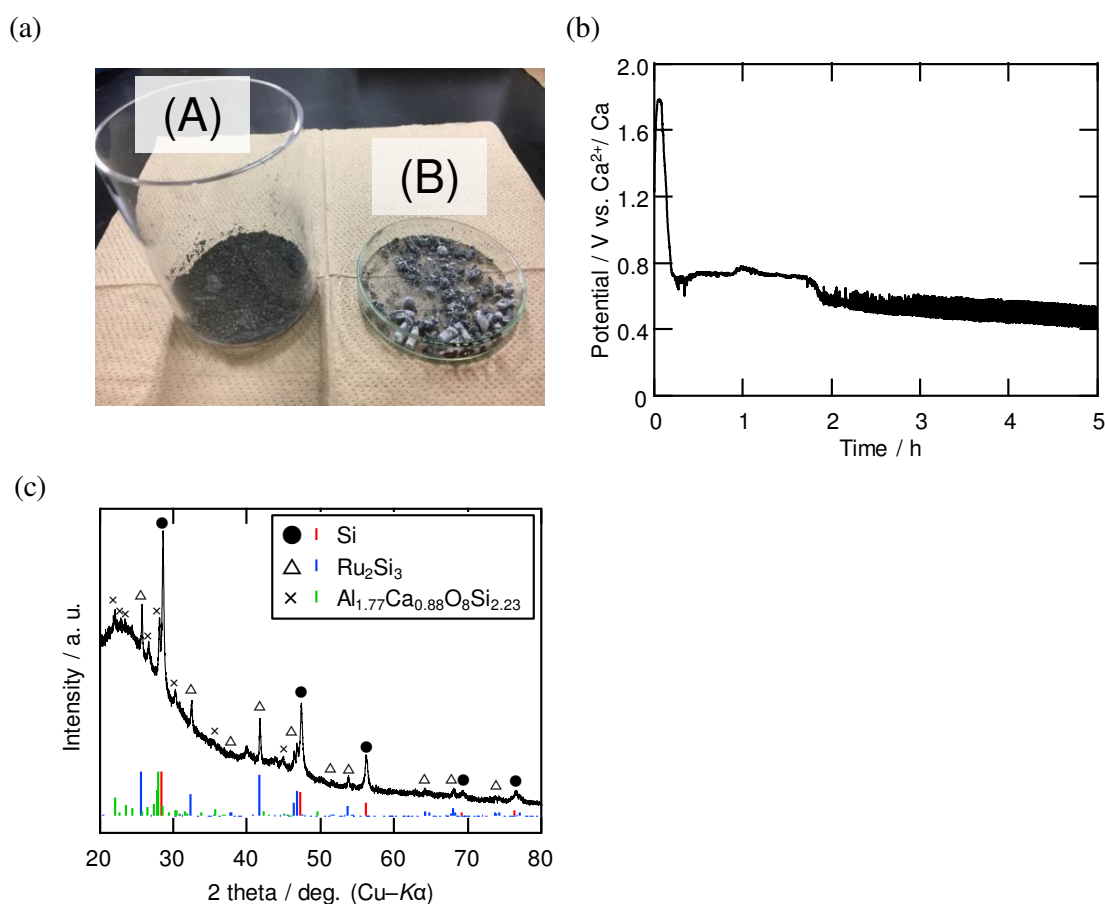


Figure 6-6 (a) A photograph of the reduction products obtained by the galvanostatic electrolysis of the simulant 3 at -2 A for 5 hours in Exp.2. (b) Transient curves of potential during electrolysis. (c) XRD pattern for the reduction product of (A).

6.3.4 Behaviors of the constituent elements during immersion and electrolysis

The distribution of elements during the electrolysis of simulant 3 was analyzed for the two samples collected: the immersed or reduction glass and the molten salt. Table 6-2 shows the element distribution for the solid phase and the molten salt in Exp. 1 and Exp. 2, which was standardized by the amount of elements in simulant 3 used in these experiments. Because CaCl_2 used as the electrolytic bath contained Sr 0.008wt% as an impurity, its behavior can be investigated only in Exp. 2. An analysis for P was not conducted owing to the difficulties implied for ICP–AES.

Comparison of element behaviors between immersion and electrolysis

First, the dissolution behaviors were analyzed from the results of the comparisons between immersion and reduced samples. In Exp. 1, several elements were different. For instance, B had a small ratio in the solid phase after immersion, but more than 80% after electrolysis. Boron was expected to be dissolved into the molten salt only during immersion. On the other hand, during electrolysis, a relatively large amount of B in the solid phase remained, which resulted in the formation of B compounds, such as CaB_6 and XB_6 ($\text{X}=\text{REE}$). These were confirmed by XRD, as shown in Figure 6-4(a). Regarding Zn, Mo, Mn, Te, Ag, Ni, and Se, whose chlorides and oxides are stable as either gases or liquids at positive potentials, they partially dissolved into the molten salt or evaporated from the system during immersion. Their ratio increased during electrolysis because their elemental form or their calcium compounds were stable in their solid states at negative potentials. While the dissolution of the Cs content in the core of simulant 3 was slow during immersion, it was facilitated after the decomposition of the Si–O network structure. Only the distributions of Ru and Rh are uncertain because of coprecipitation of Ru and Rh with CaF_2 and fluoride during dissolution by the HF solution. Their staying in solid state via the formation of Ru_2Si_3 was experimentally confirmed by XRD after electrolysis and thermodynamic calculations.

Secondly, the distribution of elements between the molten salt and the solid phase was analyzed. Figure 6-7 plots the distributions in (a) Exp. 1 and (b) Exp. 2, which are also listed in

[Table 6-2](#). For Exp. 1, the molten salt was analyzed after five batches of immersion and five batches of electrolysis. The total amounts of simulant 3 used were 0.8812 g and 9.77 g in Exp. 1 and Exp. 2, respectively. The mass ratios of CaCl_2 (450 g in Exp. 1, 200 g in Exp. 2) to simulant 3 were 511 and 21 in Exp. 1 and Exp. 2, respectively.

The behavior of elements will now be discussed by categorizing them into six groups: (1) alkali and alkaline earth elements, (2) Si, B, Al, and Zr, (3) REEs, (4) precious metal elements, (5) Se, Te, and Zn, and (6) other transition elements.

Table 6-2 Results of ICP-AES and -MS analyses for the solid phase and molten salt obtained in Exp. 1 and Exp. 2.

	Distribution of each element / %				
	Exp. 1 (Small crucible)			Exp. 2 (Large crucible)	
	Solid phase	Solid phase	Molten salt	Solid phase	Molten salt
	Immersion	0.6 V, 60 min	After Exp.	-2 A, 300 min	After Exp.
Si	122.5 ^a	88.8 ^a	9.7	145.2 ^b	-
Na	1.3 ^a	2.0 ^a	87.7	1.1 ^c	69.9
B	54.9 ^a	86.2 ^a	16.0	68.1 ^c	37.2
Al	115.5 ^a	90.6 ^a	9.2	92.8 ^a	-
Zn	41.2 ^a	79.7 ^a	1.4	0.7 ^c	-
Ce	67.7 ^a	77.2 ^a	21.8	111.1 ^c	0.0
Li	3.3 ^a	5.9 ^a	77.1	1.5 ^c	20.1
Gd	87.9 ^a	87.2 ^a	13.0	85.6 ^c	0.0
Zr	111.7 ^a	99.5 ^a	0.6	71.2 ^c	-
Nd	82.6 ^a	89.5 ^a	19.3	104.4 ^c	0.0
Mo	11.1 ^a	63.5 ^a	25.0	85.4 ^c	6.1
Cs	13.2 ^a	1.6 ^a	57.7	0.6 ^c	116.9
Ru	0.4 ^b	72.5 ^b	0.1	86.9 ^b	-
Ba	6.6 ^a	12.5 ^a	87.3	2.6 ^a	117.5
Pd	76.5 ^a	132.0 ^a	4.7	100.5 ^b	-
Pr	78.7 ^a	87.5 ^a	20.6	104.8 ^c	0.0
La	75.1 ^a	85.7 ^a	28.8	117.7 ^c	0.0
Mn	32.7 ^a	71.7 ^a	60.8	79.4 ^a	-
Sr	6.0 ^a	13.6 ^a	-	1.7 ^a	132.1
Sm	89.2 ^a	91.3 ^a	21.4	77.1 ^c	0.0
Fe	110.1 ^a	110.9 ^a	56.6	106.8 ^c	-
Y	87.3 ^a	87.5 ^a	30.2	61.8 ^c	0.0
Te	54.5 ^a	90.2 ^a	13.5	93.3 ^b	-
Rb	4.7 ^a	1.4 ^a	73.9	0.6 ^c	117.6
Rh	19.0 ^b	93.6 ^b	2.2	85.9 ^c	-
Eu	100.4 ^a	83.5 ^a	35.0	99.1 ^c	0.2
Sn	96.2 ^a	99.9 ^a	0.8	65.8 ^b	-
Ag	-	59.3 ^a	152.4	143.9 ^a	-
Ni	65.7 ^a	495.7 ^a	13557.4	92.2 ^c	-
Se	28.7 ^a	54.1 ^a	27.3	13.3 ^c	4.8
Cr	128.4 ^a	199.4 ^a	64.9	251.7 ^c	-

- : Not detected or decreased by electrolysis

a: Dissolution by Stirring in 3 M HCl solution. For the residue, dissolution by HF+HNO₃.

b: Microwave decomposition in HNO₃+HCl+HF.

c: Microwave decomposition in HNO₃+HCl. For the residue, microwave decomposition in HNO₃+HCl+HF.

Group 1: Alkali and alkali earth elements (Li, Na, Rb, Cs, Sr, and Ba)

These elements, which include one of the LLFPs (Cs), were dissolved into the CaCl_2 molten salt both in Exps. 1 and 2, which is consistent with the thermodynamic prediction discussed in Chapter 2. The only discrepancy found was the small distribution ratio of Li into the molten salt in Exp. 2. Lithium might have been intercalated in the large graphite crucible used as a cathode.

Group 2: Si, B, Al, and Zr

These elements are the main components of simulant 3. Their electrochemical reduction behavior in CaCl_2 has been already discussed in the previous researches (in Chapter 2, 3, and 5). Silicon mainly remained in the solid phase and slightly dissolved into molten CaCl_2 both in Exps. 1 and 2. Boron remained in the solid phase, but partially dissolved into CaCl_2 . The dissolution ratio of B was larger in Exp. 2 than in Exp. 1. Because calcium borates are stable for low $p\text{O}^{2-}$ values, as shown in the potential– $p\text{O}^{2-}$ diagram for the B–Ca–O–Cl system (Figure 2-4), they were partially dissolved, particularly borate ions ($\text{B}_2\text{O}_4^{2-}$) in the O^{2-} -abundant electrolyte used in Exp. 2. On the other hand, almost all of the Al and Zr remained in the solid phase.

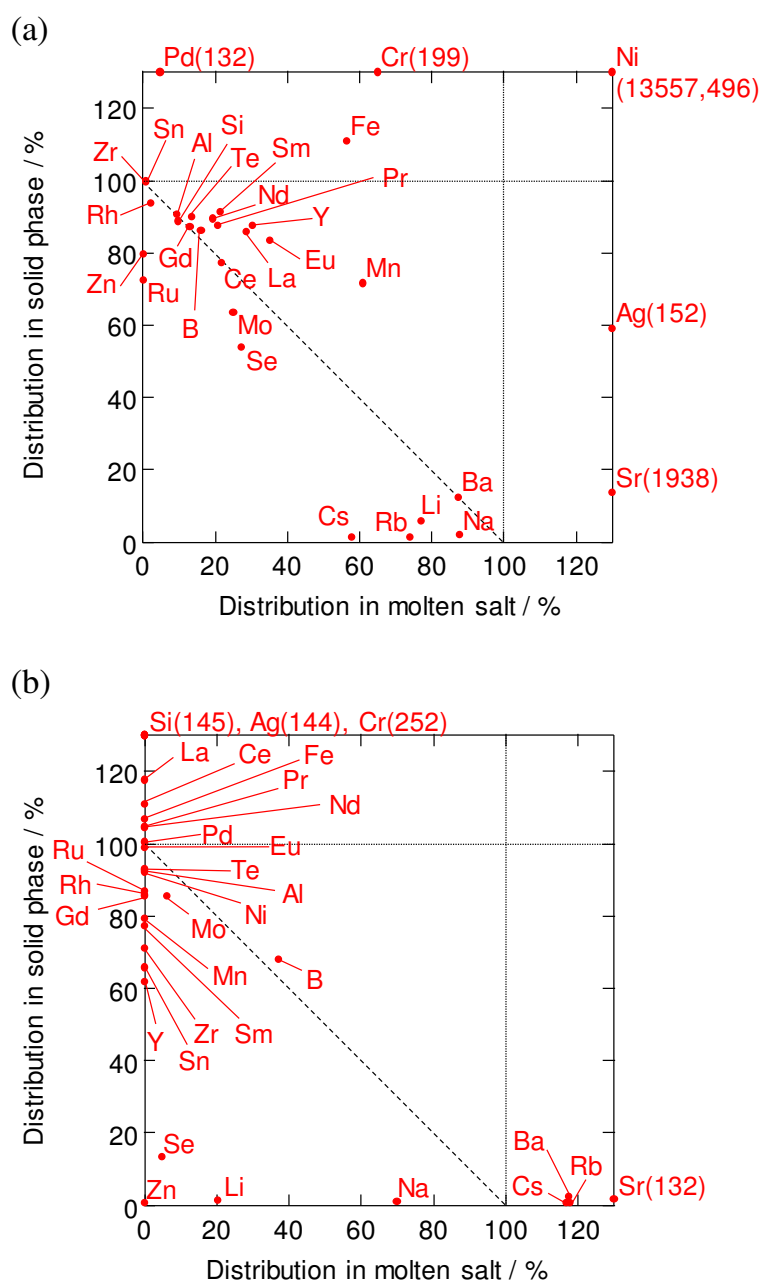


Figure 6-7 (a) Plot for distribution of elements to molten salt vs. solid phase from ICP-AES/MS analysis results in Exp.1 and (b) in Exp.2.

Group 3: Rare earth elements (*Y, La, Ce, Pr, Nd, Sm, Eu, and Gd*)

The behaviors of these elements has already been discussed and the formation of XB_6 ($\text{X}=\text{REE}$) was confirmed, as explained in Section 6.3.2. In Exp. 1, all of the REEs remained in the solid products and partially dissolved into CaCl_2 , up to 35%. In Exp. 2, they were not detected at all in the molten salt. The dissolution of alkali oxides and alkaline earth oxides caused the formation of stable REE oxides or oxychlorides, whose reduction presents difficulties even at 0.6 V and especially in Exp. 2. Thus, the formation of XB_6 and the dissolution of REEs in molten salt was not confirmed in Exp. 2.

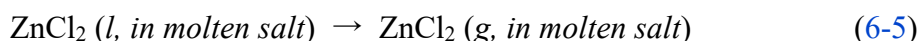
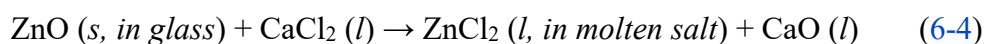
Group 4: Precious metal elements (*Ru, Rh, Pd, and Ag*)

These elements, which include one of the LLFPs (Pd), were stable in their metallic state and were detected in the solid phase. This behavior is in good agreement with the potential– $p\text{O}^{2-}$ diagrams (Figure 2-13). The detection of Ag in the molten salt in Exp. 1 was caused by the Ag^+/Ag reference electrode.

Group 5: *Se, Te, and Zn*

Selenium is one of the LLFPs. Se and Te are both chalcogen elements, but their behaviors are quite different. The evaporation of Se and Zn from the system had already been reported in Chapter 5.

Because some compounds, such as $\text{Se}_2(\text{g})$, $\text{SeO}_2(\text{g})$, and $\text{ZnCl}_2(\text{g})$, are volatile, the distributions in both the solid phase and the molten salt were small for Zn and Se. According to Figure 2-2 and Figure 2-8, ZnO reacted with CaCl_2 to produce ZnCl_2 with low activity in the dissolved state in the molten salt. Then, the ZnCl_2 evaporated into the gas phase.



The selenium species were possibly removed as Se₂ gas at the anode (Equation 6-6). The Se²⁻ ions were generated from the dissolution of CaSe₂, which formed during electrolysis.



The distribution ratio of Se and Zn was relatively large in Exp. 1 owing to the short duration time of the electrolysis. A detailed discussion for Zn and Se has been already in Chapter 5.

ICP results show that Te mostly stayed in the solid phase. From the potential- $p\text{O}^{2-}$ diagrams (Figure 2-14), Te was expected to remain as metallic Te(*l*) or a CaTe(*s*) intermetallic compound.

Group 6: Other transition elements (Cr, Mn, Fe, Ni, and Mo)

These elements are in the transition metals group and had relatively large stable regions of their elemental state in the potential- $p\text{O}^{2-}$ diagrams (Figure 2-15) for potentials more negative than *ca.* 1.0 V vs. Ca²⁺/Ca. Partial distributions of Mo and Mn were found in the molten salt in Exp. 1, while transition elements were detected only in the solid phase except for Mo in Exp. 2. They were stable in the solid state, especially for low $p\text{O}^{2-}$ values. The small amounts of dissolution of Mo and Mn in the molten salt in Exp. 1 resulted from reactions during immersion. More concretely, although these oxides can be dissolved into the melt, they are easily reduced to their metallic state without dissolution. The partial dissolution of Mo into the molten salt can be also explained by the dissolution of oxides or calcium molybdates, not of Mo in its metallic state. From Figure 2-15(e), it can be seen that several compounds are stable in their gas state. Thus, Mo compounds have the possibility to partially evaporate from the system during long electrolysis processes. As for Mn, oxides or chlorides stable at positive potentials may have caused the partial dissolution of Mn into the molten salt in Exp. 1.

Summary of all elements behaviors

Figure 6-8 summarizes the behavior of each element in simulant 3 after electrolysis in molten CaCl_2 . The author inferred some amounts of Zn and Se evaporated from the system. Zr and other elements (Al, B, REEs, Pd, Ru, Rh, Zn, Ag, Sn, Te, and so on) were in the solid phase. REEs mainly remained in the solid phase as metals, oxides, or oxychlorides. In some conditions, REEs formed XB_6 ($\text{X} = \text{REE}$) compounds. Precious metal elements (Ru, Rh, Pd, and Ag) remained in the solid phase in their metallic state. Some elements formed Si alloys, such as Mo, Pd, Ru, and so on. Alkali and alkaline earth elements dissolved into the molten CaCl_2 . Partial dissolution into molten salt occurred for Mn, Mo, REEs, and Se, depending on the $p\text{O}^{2-}$ value.

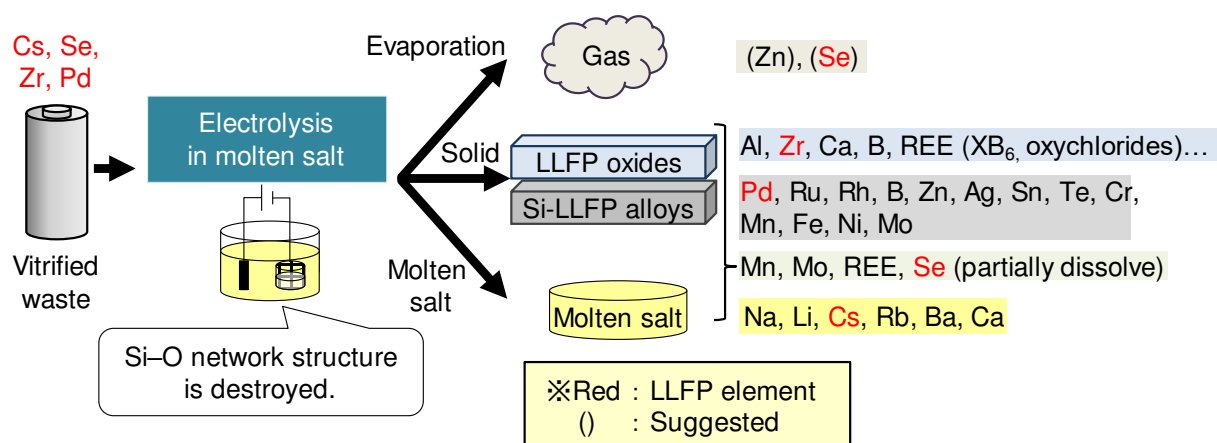


Figure 6-8 Behavior of the elements during the electrochemical reduction of the simulant 3 in molten CaCl_2 .

6.4 Conclusion

The electrochemical reduction behavior of simulant 3, which was composed of 33 oxides including LLFP elements (Cs, Se, Zr, and Pd), was investigated in molten CaCl_2 at 1103 K, for the treatment of vitrified nuclear waste. The reduction products of potentiostatic electrolysis in a small crucible were analyzed (Exp. 1). The reduction speed was accelerated by the components in simulant 3, compared with simulant 2 (in Chapter 5). The formation of Si, CaB_6 , and XB_6 ($\text{X}=\text{REE}$) was confirmed.

After galvanostatic electrolysis of simulant 3 in molten CaCl_2 for 300 min in a large crucible, tens of grams of reduction products were obtained (Exp. 2). The formation of Si and Ru_2Si_3 was confirmed.

The behavior of elements during electrolysis was evaluated via ICP-AES and ICP-MS for both Exps. 1 and 2. In both cases, the dissolution of alkali and alkaline earth elements (including Cs) into CaCl_2 was confirmed. Precious metal elements (including Pd) stayed in the solid phase, as well as Zr. REEs partially dissolved into the molten salt at low O^{2-} concentrations in Exp. 1, and mostly remained in the solid phase at high O^{2-} concentrations in Exp. 2. These behaviors are consistent with the constructed potential– $p\text{O}^{2-}$ diagrams. Zn and Se were indicated to have partially evaporated from the system, especially when the electrolysis time was long (Exp. 2).

6.5 Reference list

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Chapter 7

General conclusions

The electrochemical reduction of vitrified nuclear waste simulants in molten CaCl_2 has been investigated with the purpose of the recovery of LLFPs from vitrified waste. Four types of simulants including a borosilicate glass whose components are simple, were electrochemically reduced in molten CaCl_2 and the behavior of constituent elements was clarified. Also, the electrochemical reduction behavior of Al_2O_3 , which is one of the major component of vitrified waste, has been investigated. In all the studies, the sealed electrode was used to conduct the cyclic voltammetry. Although some simulants had a low softening point, the electrochemical reduction experiments were successful. The obtained results are summarized below.

In Chapter 2, the electrochemical reduction behaviors of all the constituent of vitrified waste were predicted. Ellingham diagrams of oxides and chlorides, and potential– $p\text{O}^{2-}$ diagrams were constructed from the thermodynamic data. From the potential– $p\text{O}^{2-}$ diagram, the stable range of potential and $p\text{O}^{2-}$ for each compound was predicted. Also, the dissolution behavior of each element in molten CaCl_2 was predicted.

In Chapter 3, the electrochemical reduction behavior of borosilicate glass (=Pyrex[®] glass and Tempax[®] glass) in molten CaCl_2 was investigated at 1123 K. The borosilicate glass was composed of SiO_2 , B_2O_3 , Na_2O , K_2O , and Al_2O_3 . From cyclic voltammetry, B_2O_3 was indicated to be reduced at more positive potential than the reduction potential of SiO_2 . The main component of SiO_2 was reduced to Si at 0.9 and 0.6 V (vs. Ca^{2+}/Ca). XPS and Raman analysis results showed that B_2O_3 was reduced to B–Si compound at 0.9 V (vs. Ca^{2+}/Ca). Al_2O_3 was not reduced to form

Ca–Al–O compound at the same potential. Na₂O and K₂O were dissolved in molten CaCl₂. Considering the potential– pO^{2-} diagrams, the range of pO^{2-} was deduced to be 2.95–4.33 during the electrolysis of the borosilicate glass at 0.9 V.

In Chapter 4, the electrochemical reduction behavior of Al₂O₃, one of the main component of vitrified waste, was investigated. In a Mo box-type electrode, an Al₂O₃ tube was successfully reduced to liquid Al with a maximum purity of 98 at%. However, in the electrolysis of Al₂O₃ powder in an Fe box-type electrode, Al₂Ca was produced through the formation of Ca₁₂Al₁₄O₃₃ as an intermediate product. The different electrochemical reduction behaviors of the tube and the powder were explained by the different diffusion path lengths for O²⁻ ions from three-phase zone (Al₂O₃/CaCl₂/cathode metal) to bulk CaCl₂.

In Chapter 5, the electrochemical reduction of two types of simplified simulants of vitrified radioactive waste, simulant 1 (glass component only: SiO₂, B₂O₃, Na₂O, Al₂O₃, CaO, Li₂O, and ZnO) and simulant 2 (also containing long-lived fission product oxides, ZrO₂, Cs₂O, PdO, and SeO₂), was investigated in molten CaCl₂ at 1103 K. After the immersion of simulant 1 into molten CaCl₂ without electrolysis, the dissolution of Na, Li, and Cs into molten salt was confirmed by ICP-AES and -MS analysis of the samples. After simulants 1 and 2 were electrolyzed at 0.9 V vs. Ca²⁺/Ca, the SEM/EDX and XRD analysis confirmed that most of SiO₂ had been reduced to Si. After the electrolysis, Al, Zr, and Pd remained in the solid phase. SeO₂ was found to partially remain in the solid phase and partially evaporate. In addition, a small quantity of SeO₂ dissolved into the molten salt.

In Chapter 6, the electrochemical reduction of vitrified nuclear waste simulant composed of 33 oxides, which is called simulant 3, was investigated in molten CaCl₂ at 1103 K. In the first experiment, the small crucible electrodes containing *ca.* 100 mg of simulant 3 were electrolyzed at 0.6–1.1 V vs. Ca²⁺/Ca. XRD analysis confirmed that SiO₂, which was the main component of simulant 3, was reduced to Si. Formations of Ru₂Si₃ and XB₆ (X = Ca or rare earth elements (REEs)) were also indicated. In the second experiment, the large crucible electrode containing *ca.*

10 g of simulant 3 was galvanostatically electrolyzed at 2 A for 300 min. The distribution ratios of the constituent elements in the solid reduced product and the molten salt were calculated by the composition analysis using ICP-AES and ICP-MS. As the results, alkali and alkaline earth elements including Cs were dissolved into molten salt. REEs mostly remained in the solid reduced product. Most of the other elements including Zr and Pd were found in the solid product. Se and Zn were indicated to partially evaporate, depending on the duration time of electrolysis.

Based on the results especially in Chapter 6, the behaviors of constituent elements of vitrified nuclear wastes are summarized as Figure 7-1. One of the main purposes of this study is the clarification of behaviors of LLFPs (Zr, Pd, Cs, and Se). Zr stays in the solid phase as the oxides. Pd remains in the solid phase as a metallic state. Cs dissolves into the molten salt. Se is expected to be partially dissolved into molten salt and partially evaporated. The amount of evaporation is supposed to increase in the case of a long-term electrolysis.

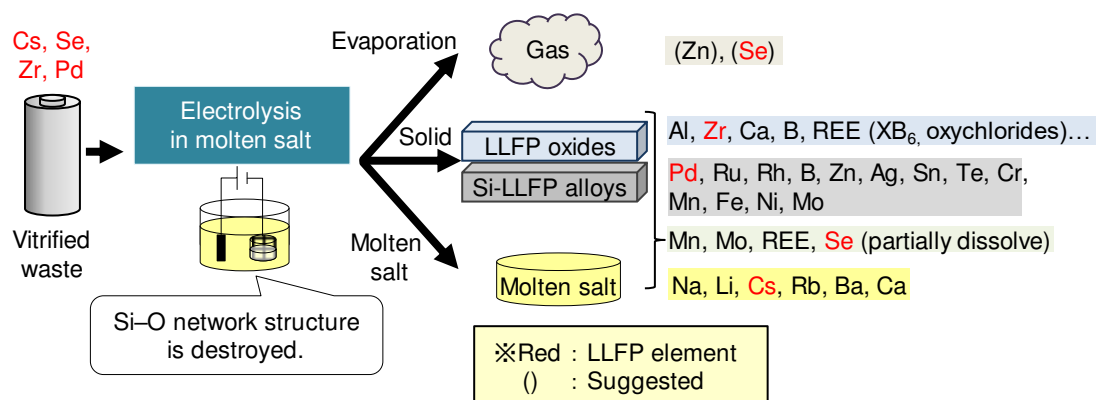


Figure 7-1 Behaviors of the constituent elements during the electrochemical reduction of the vitrified nuclear waste in molten CaCl_2 .

To avoid passing nuclear wastes, *i.e.*, the negative legacy to the future, people are waiting for the technology to decrease the amount of radioactive of nuclear waste. The knowledge obtained in this study is concerning just a part of the whole process. In the future, further development of the process is necessary. One of the challenges is the recovery of Cs from molten salt. The refreshment of molten salt is supposed during the process. After the recovery of molten salt, the elemental Cs is expected to be collected by cathodic reaction. Since the reduction potential of Cs is very negative, the highly efficient recovery of Cs is thought to be difficult. In this study, Pd and Zr are in the solid phase, but their chemical states are deduced from the thermodynamic calculations. Also, many other elements remain in the solid phase. Further development of other separation processes is required in addition to the analysis of chemical states of Pd and Zr. Se is indicated to be partially evaporated because Se^{2-} ions are oxidized to Se_2 gas at the anode. The collection method of the evolved Se_2 gas should be studied in the future.

In the end, I hope the problem of nuclear waste disposal will be solved in the future.

List of Publications

The main parts of this thesis are constructed from the following papers.

Chapter 2

The thermodynamic calculations are separately published in the following papers.

Chapter 3

1. Y. Katasho, X. Yang, K. Yasuda and T. Nohira

Journal of the Electrochemical Society, **163**(10), D622–D627 (2016).

“Electrochemical Reduction Behavior of Borosilicate Glass in Molten CaCl_2 ”

2. Y. Katasho, K. Yasuda and T. Nohira

Journal of the Electrochemical Society, **164**(7), D478–D485 (2017).

“Behaviors of Si, B, Al, and Na during Electrochemical Reduction of Borosilicate Glass in Molten CaCl_2 ”

*** Journal of the Electrochemical Society Editors' Choice article (2017) ***

Chapter 4

3. H. Kadowaki, Y. Katasho, K. Yasuda and T. Nohira,

Journal of the Electrochemical Society, **165**(2), D83–D89 (2018).

“Electrolytic Reduction of Solid Al_2O_3 to Liquid Al in Molten CaCl_2 ”

Chapter 5

4. Y. Katasho, K. Yasuda and T. Nohira,

Journal of Nuclear Materials, accepted.

“Electrochemical Reduction Behavior of Simplified Simulants of Vitrified Radioactive Waste in Molten CaCl_2 ”

Chapter 6

5. Y. Katasho, K. Yasuda and T. Nohira,

Journal of Nuclear Materials, to be submitted.

“Electrochemical Reduction Behavior of Vitrified Nuclear Waste Simulant in Molten CaCl_2 ”

Appendix

A. Potential– pO^{2-} diagrams drawing with a software for chemical potential diagrams

The calculated potential– pO^{2-} diagrams in Chapter 2 were cross-checked with the ones which are drawn by a software for creating chemical 3-D potential diagrams, Chesta ver. 3.2.6.9 [1]. Following figures are the all used 3-D potential diagrams and potential– pO^{2-} diagrams drawn by Chesta. The same thermodynamic data was used to construction the 3-D potential diagrams.

Reference list

- [1] N. Hatada, Chesta ver. 3.2.6.9 (2014).
<http://www.aqua.mtl.kyoto-u.ac.jp/chestaEng.html>.

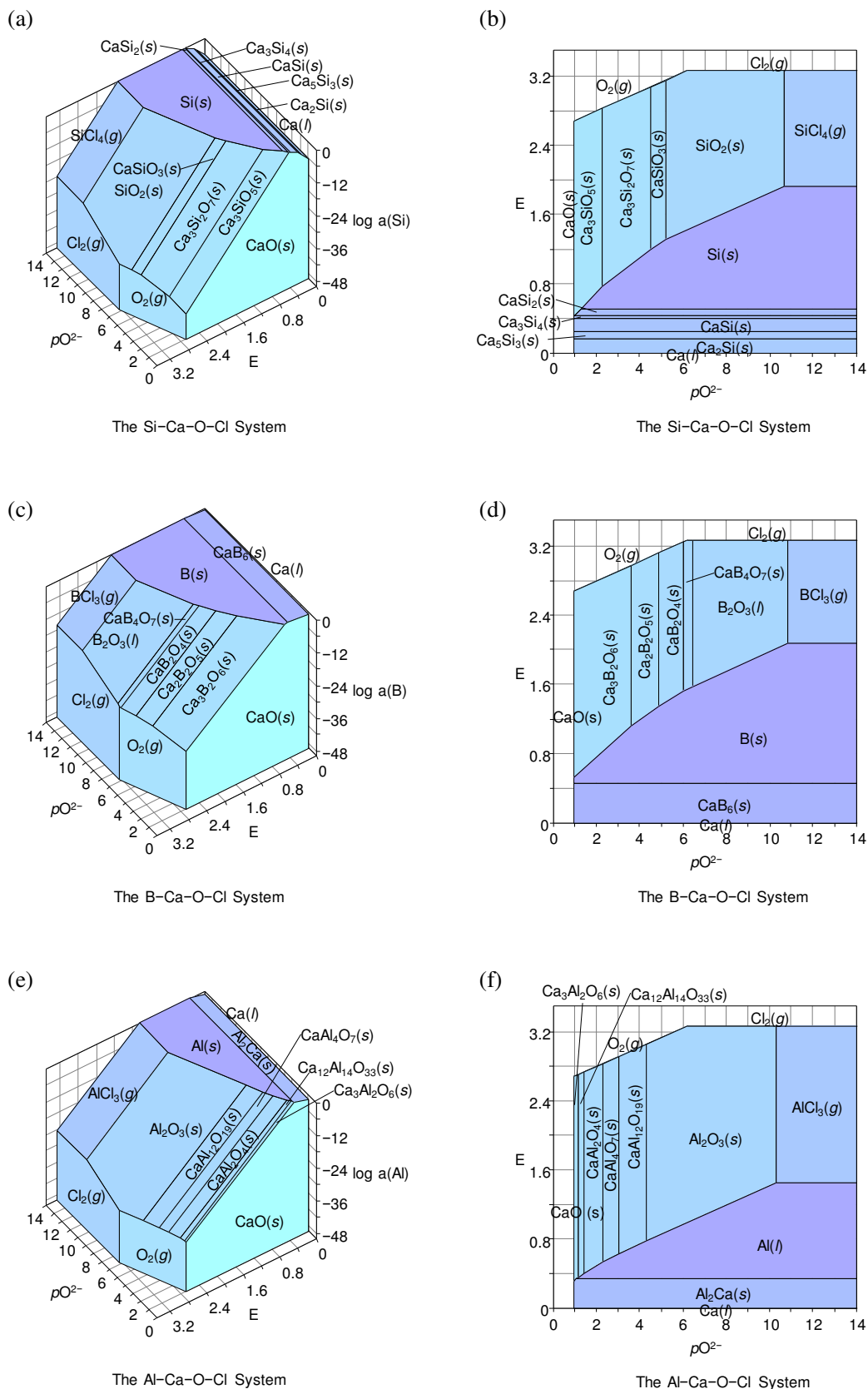


Figure A-1 Potential- pO^{2-} diagrams (a) with $\log a(\text{Si})$, (b) projected figure for Si-Ca-O-Cl system, (c) with $\log a(\text{B})$, (d) projected figure for B-Ca-O-Cl system, and (e) with $\log a(\text{Al})$, (f) projected figure for Al-Ca-O-Cl system in molten CaCl_2 at 1123 K.

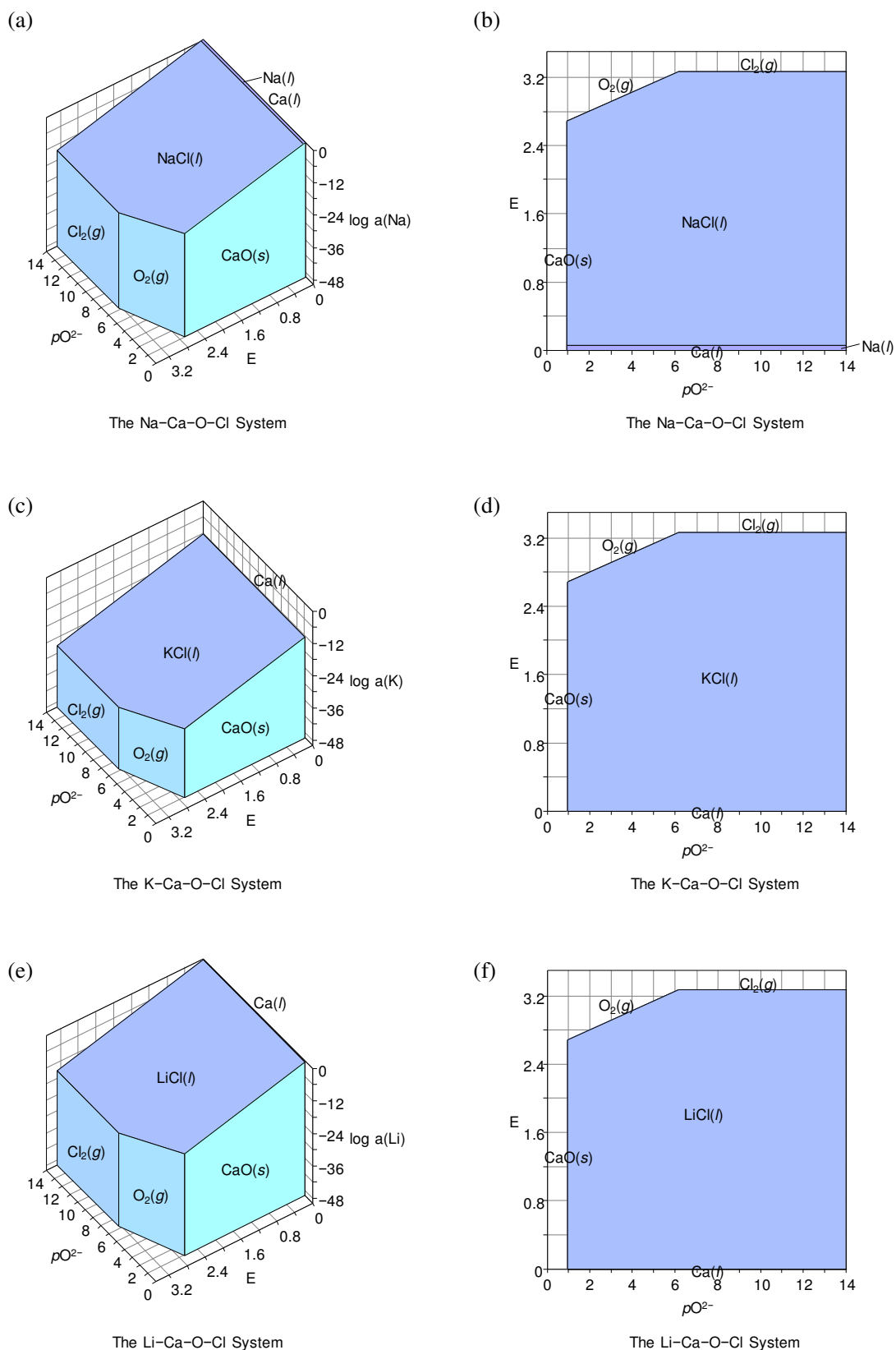


Figure A-2 Potential- pO^{2-} diagrams (a) with $\log a(\text{Na})$, (b) projected figure for Na-Ca-O-Cl system, (c) with $\log a(\text{K})$, (d) projected figure for K-Ca-O-Cl system, and (e) with $\log a(\text{Li})$, (f) projected figure for Li-Ca-O-Cl system in molten CaCl_2 at 1123 K.

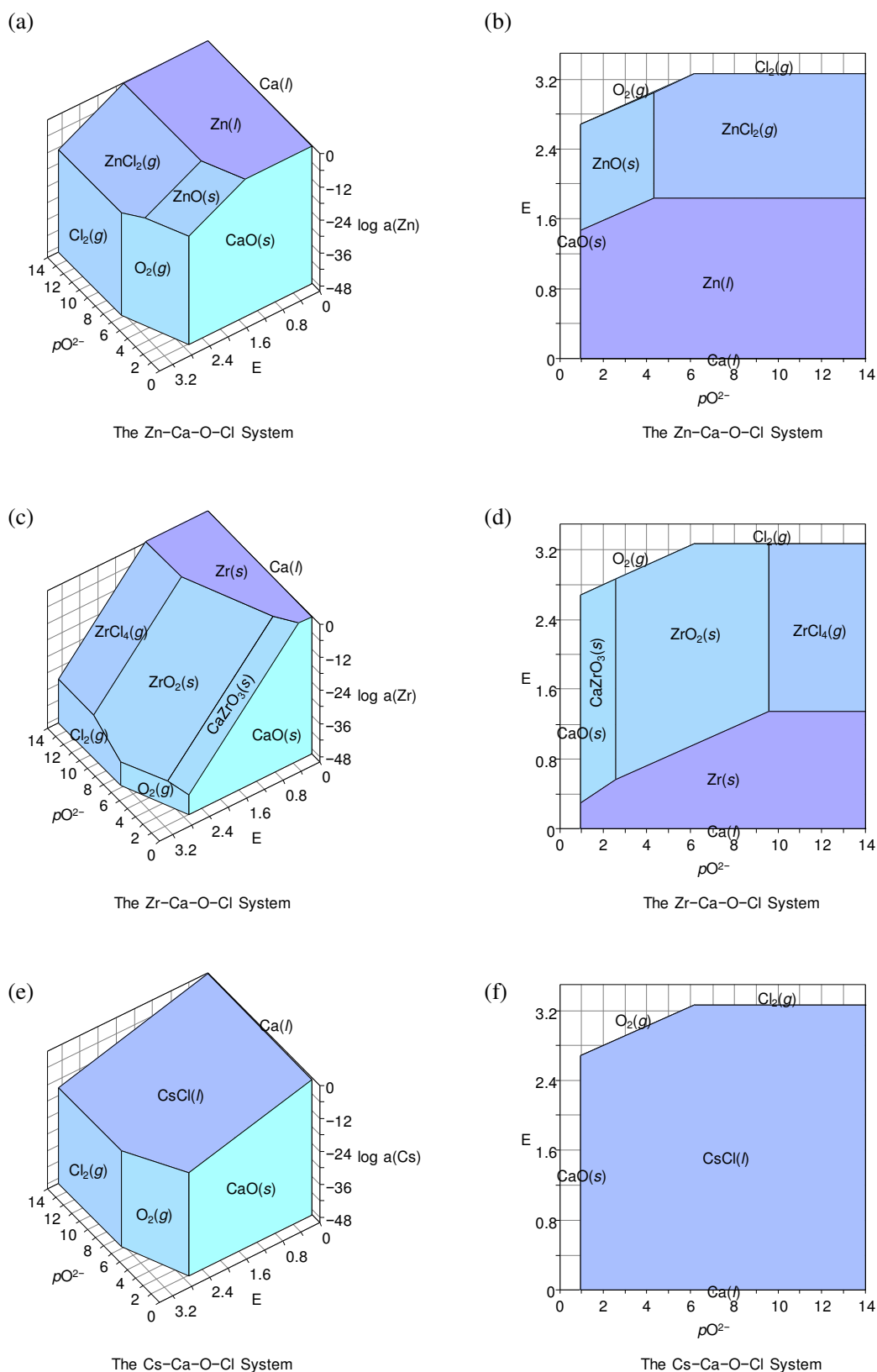


Figure A-3 Potential- pO^{2-} diagrams (a) with $\log a(Zn)$, (b) projected figure for Zn-Ca-O-Cl system, (c) with $\log a(Zr)$, (d) projected figure for Zr-Ca-O-Cl system, and (e) with $\log a(Cs)$, (f) projected figure for Cs-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

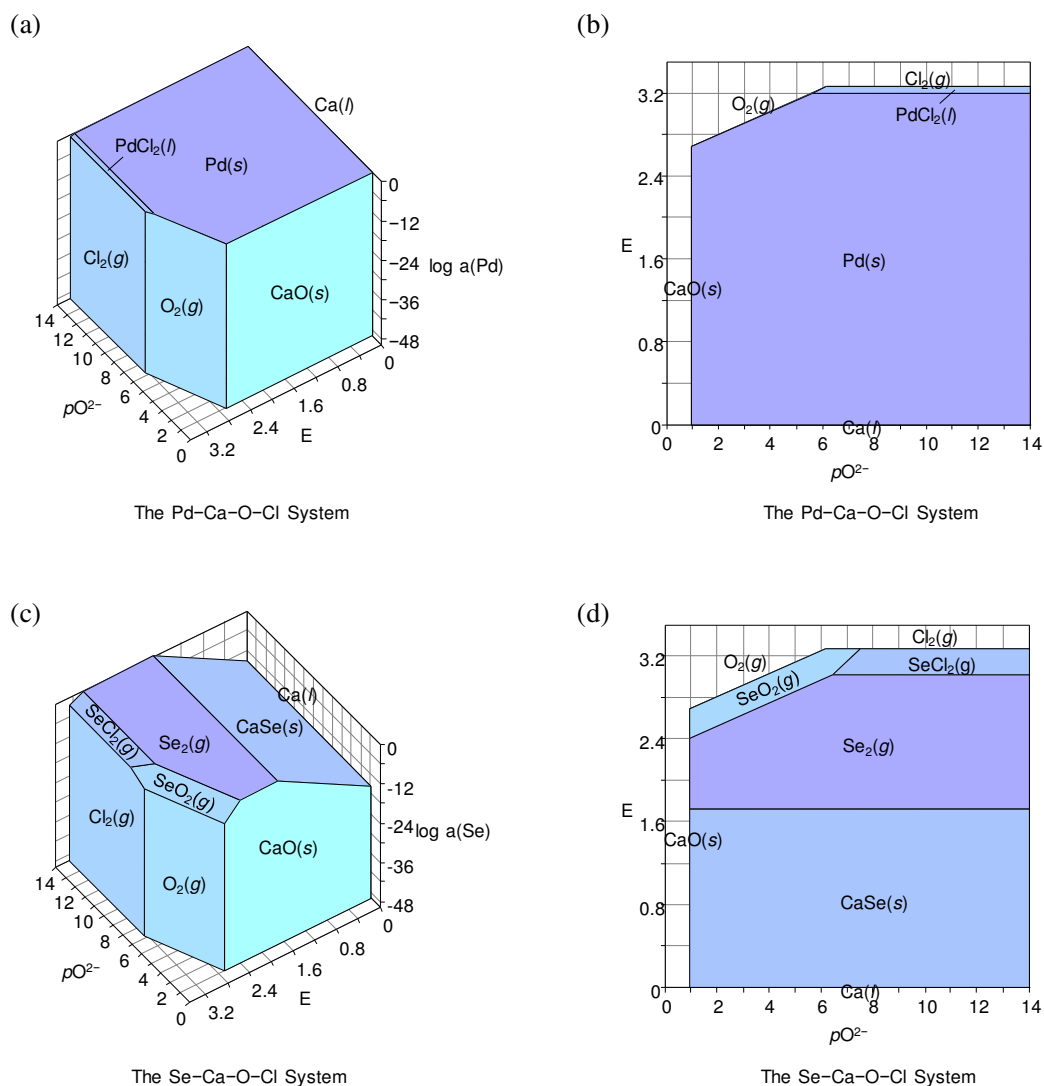


Figure A-4 Potential- pO^{2-} diagrams (a) with $\log a(Pd)$, (b) projected figure for Pd-Ca-O-Cl system, (c) with $\log a(Se)$, and (d) projected figure for Se-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

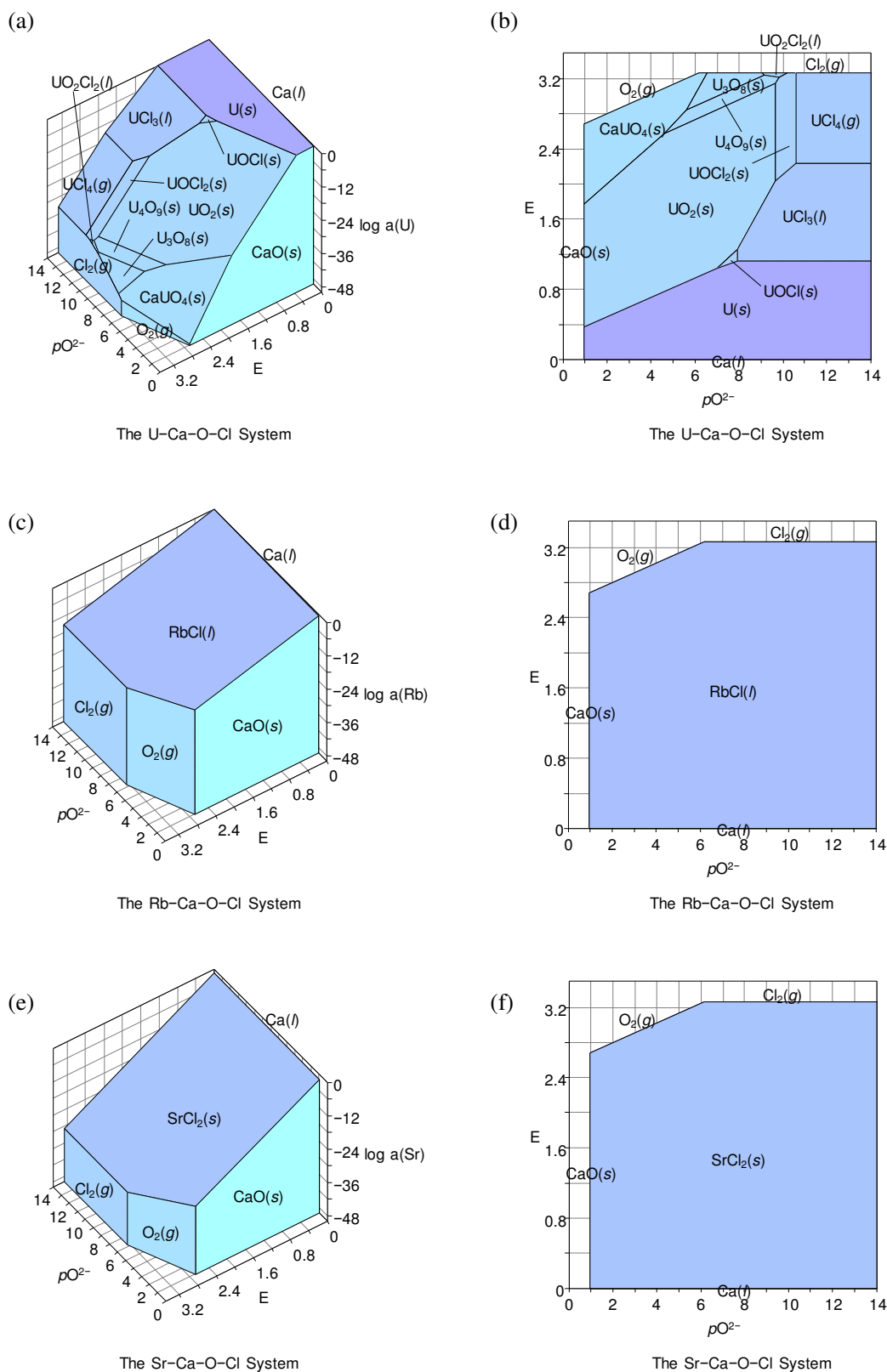


Figure A-5 Potential- pO_2^- diagrams (a) with $\log a(U)$, (b) projected figure for U-Ca-O-Cl system, (c) with $\log a(Rb)$, (d) projected figure for Rb-Ca-O-Cl system, and (e) with $\log a(Sr)$, (f) projected figure for Sr-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

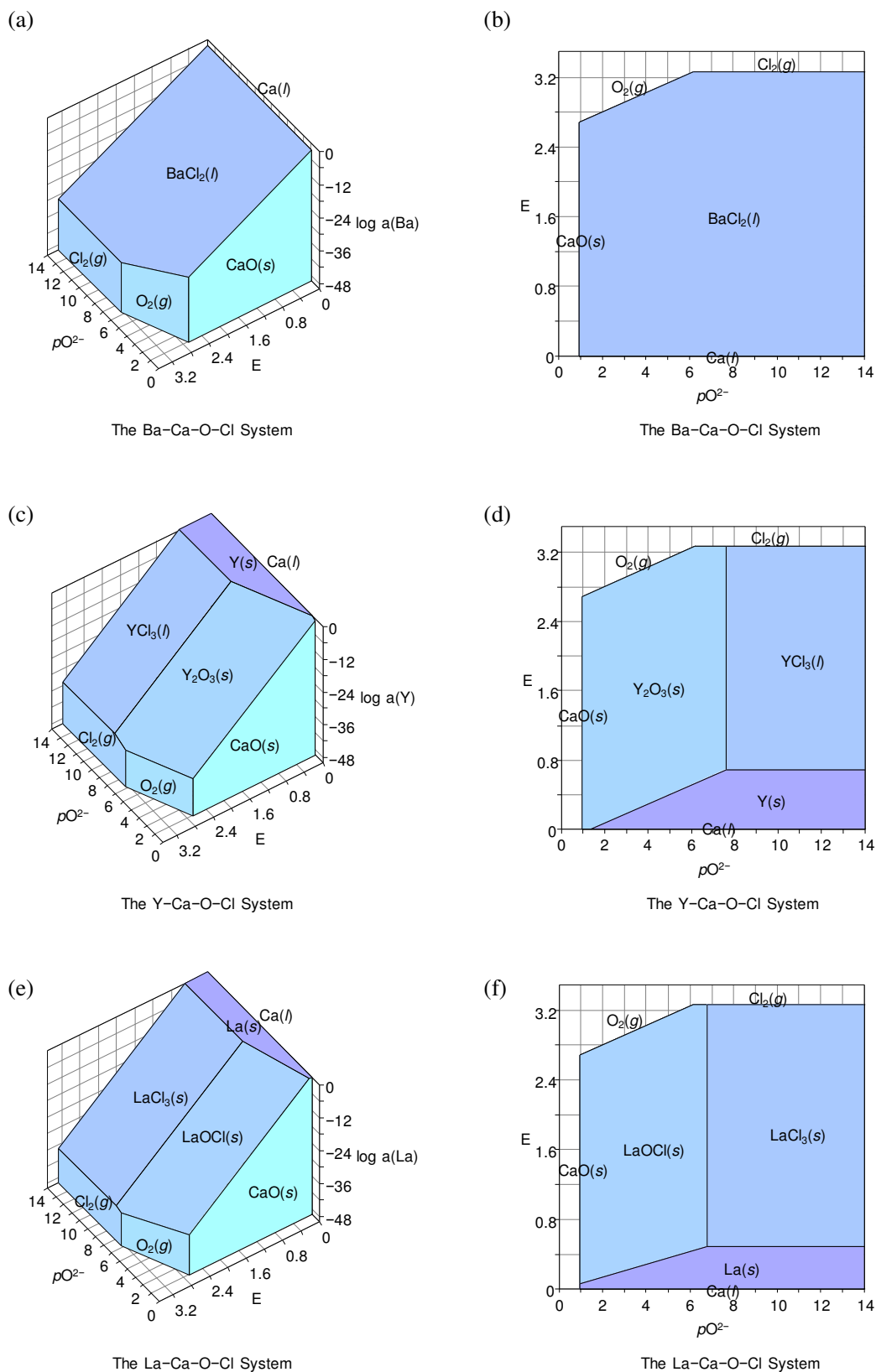


Figure A-6 Potential- pO^{2-} diagrams (a) with $\log a(\text{Ba})$, (b) projected figure for Ba-Ca-O-Cl system, (c) with $\log a(\text{Y})$, (d) projected figure for Y-Ca-O-Cl system, and (e) with $\log a(\text{La})$, (f) projected figure for La-Ca-O-Cl system in molten CaCl_2 at 1123 K.

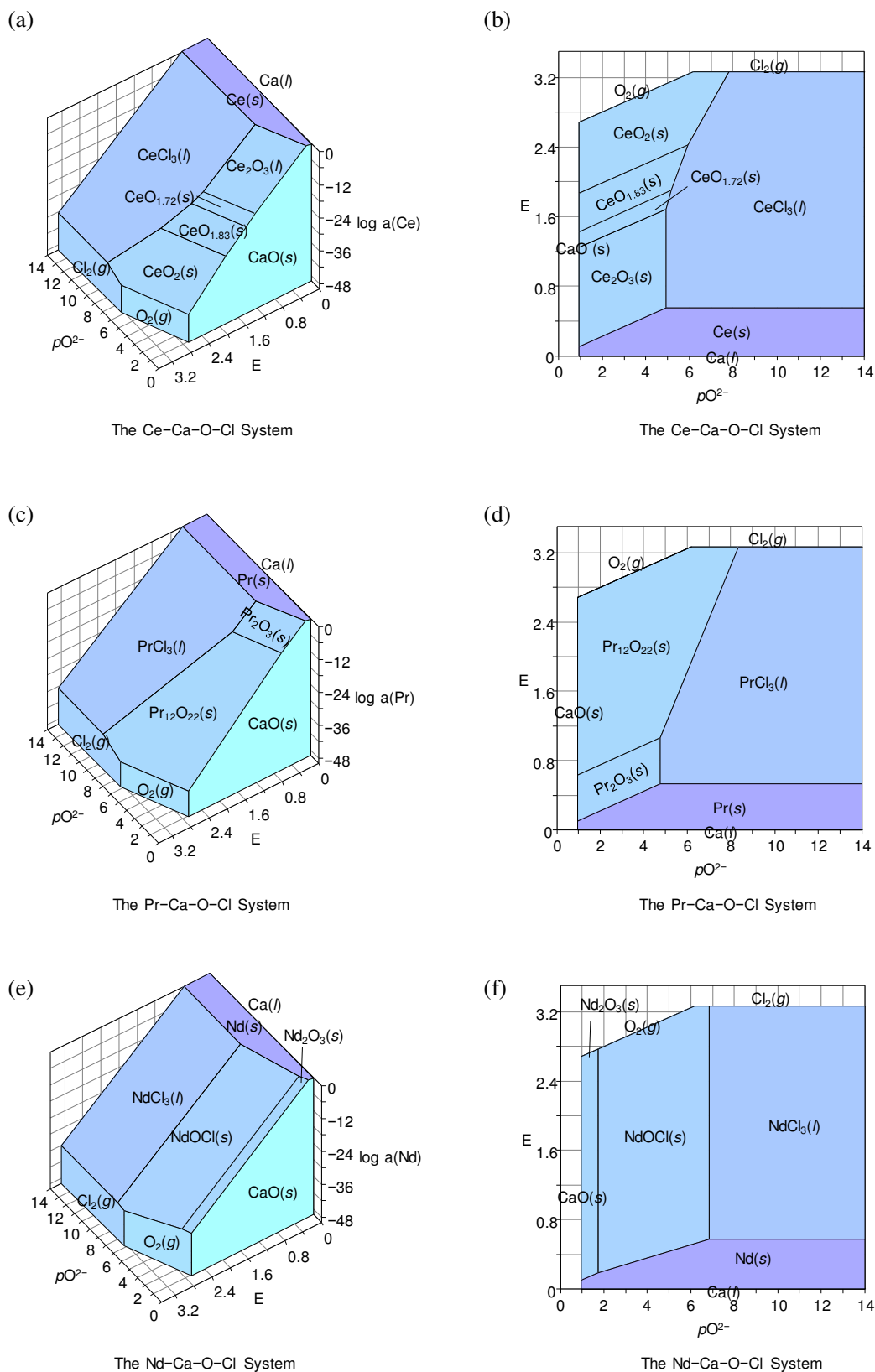


Figure A-7 Potential- pO^{2-} diagrams (a) with $\log a(\text{Ce})$, (b) projected figure for Ce-Ca-O-Cl system, (c) with $\log a(\text{Pr})$, (d) projected figure for Pr-Ca-O-Cl system, and (e) with $\log a(\text{Nd})$, (f) projected figure for Nd-Ca-O-Cl system in molten CaCl_2 at 1123 K.

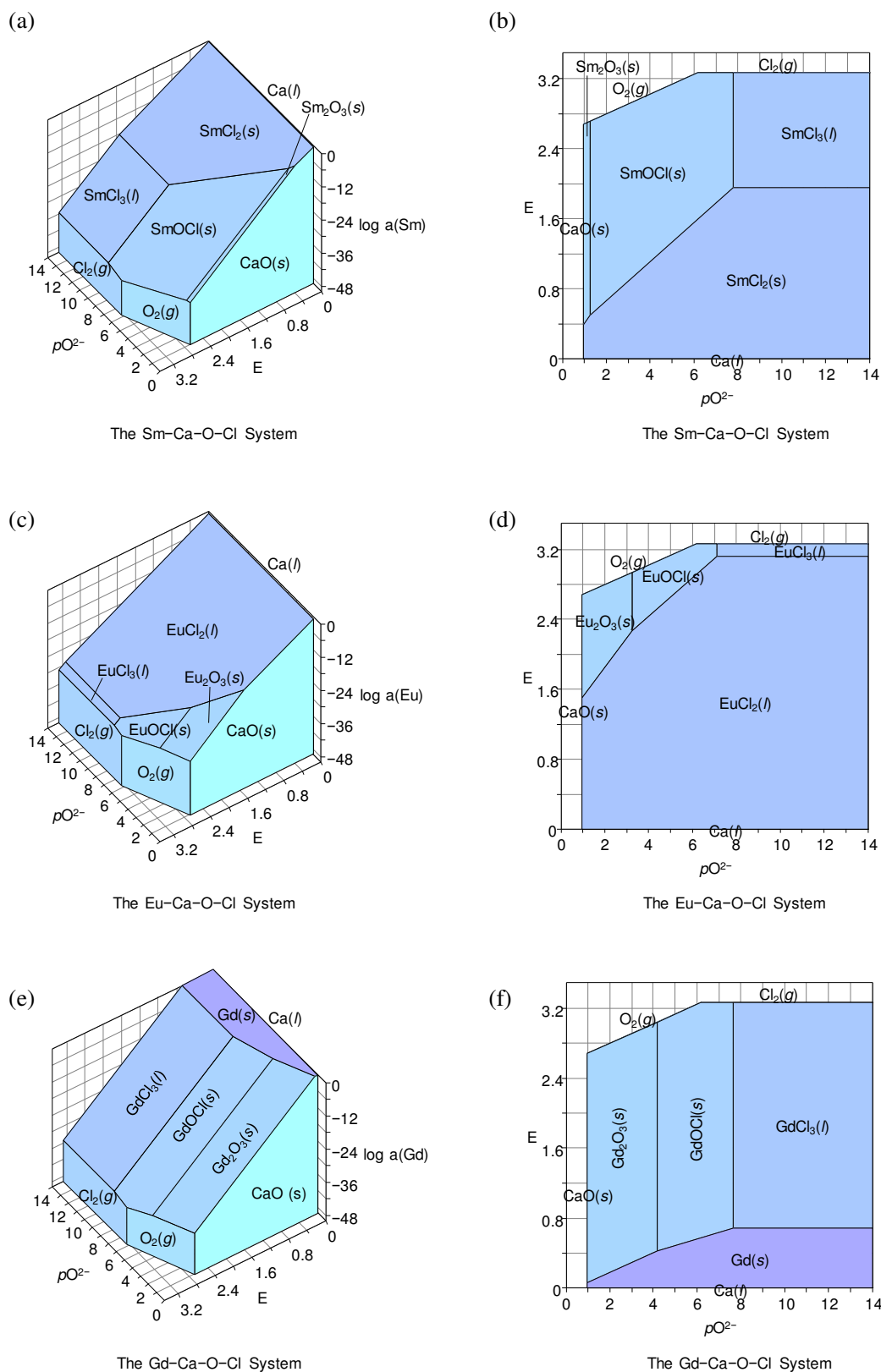


Figure A-8 Potential- pO^{2-} diagrams (a) with $\log a(\text{Sm})$, (b) projected figure for Sm-Ca-O-Cl system, (c) with $\log a(\text{Eu})$, (d) projected figure for Eu-Ca-O-Cl system, and (e) with $\log a(\text{Gd})$, (f) projected figure for Gd-Ca-O-Cl system in molten CaCl_2 at 1123 K.

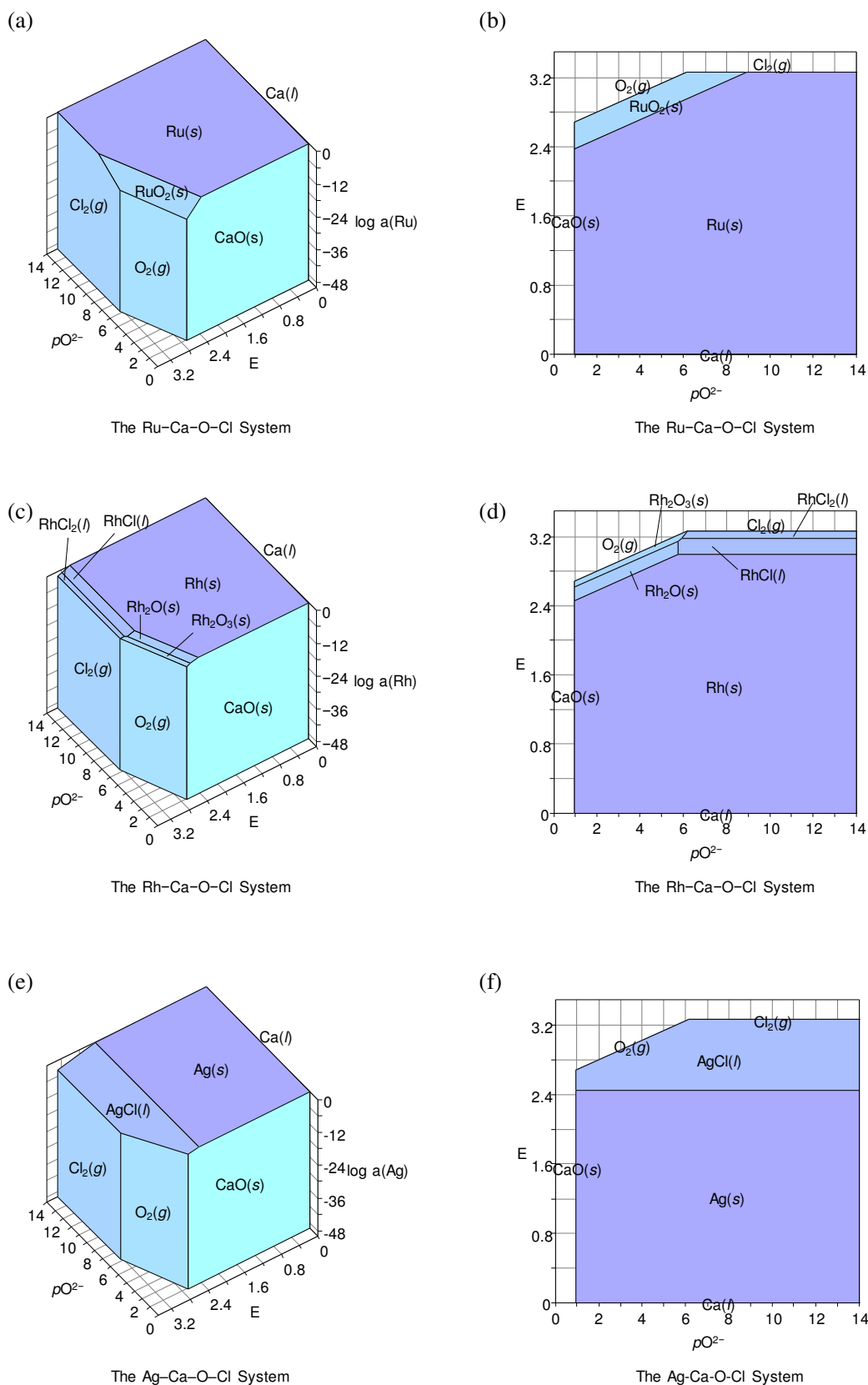


Figure A-9 Potential- pO^{2-} diagrams (a) with $\log a(Ru)$, (b) projected figure for Ru-Ca-O-Cl system, (c) with $\log a(Rh)$, (d) projected figure for Rh-Ca-O-Cl system, and (e) with $\log a(Ag)$, (f) projected figure for Ag-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

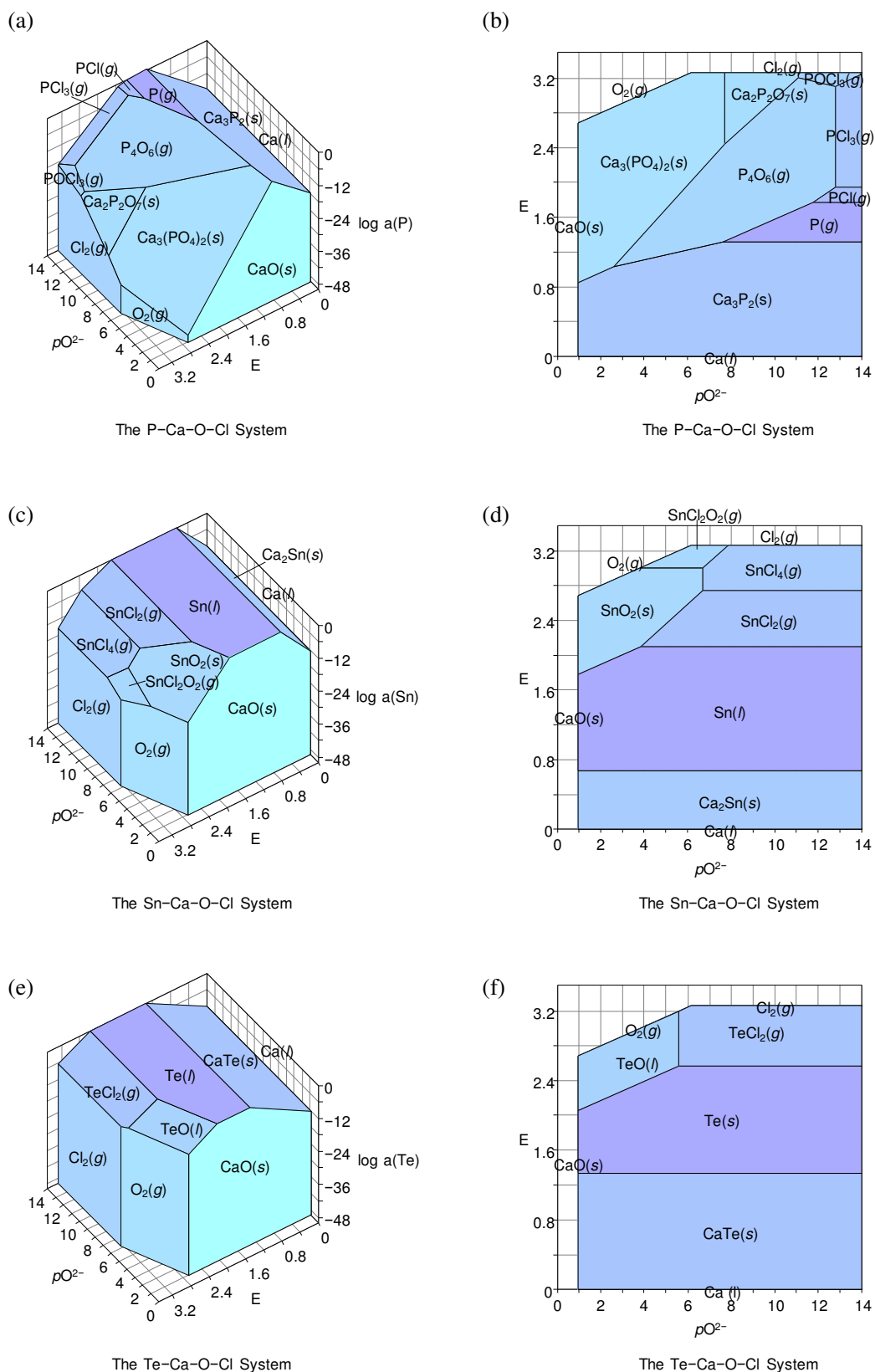


Figure A-10 Potential- pO^{2-} diagrams (a) with $\log a(P)$, (b) projected figure for P-Ca-O-Cl system, (c) with $\log a(Sn)$, (d) projected figure for Sn-Ca-O-Cl system, and (e) with $\log a(Te)$, (f) projected figure for Te-Ca-O-Cl system in molten $CaCl_2$ at 1123 K.

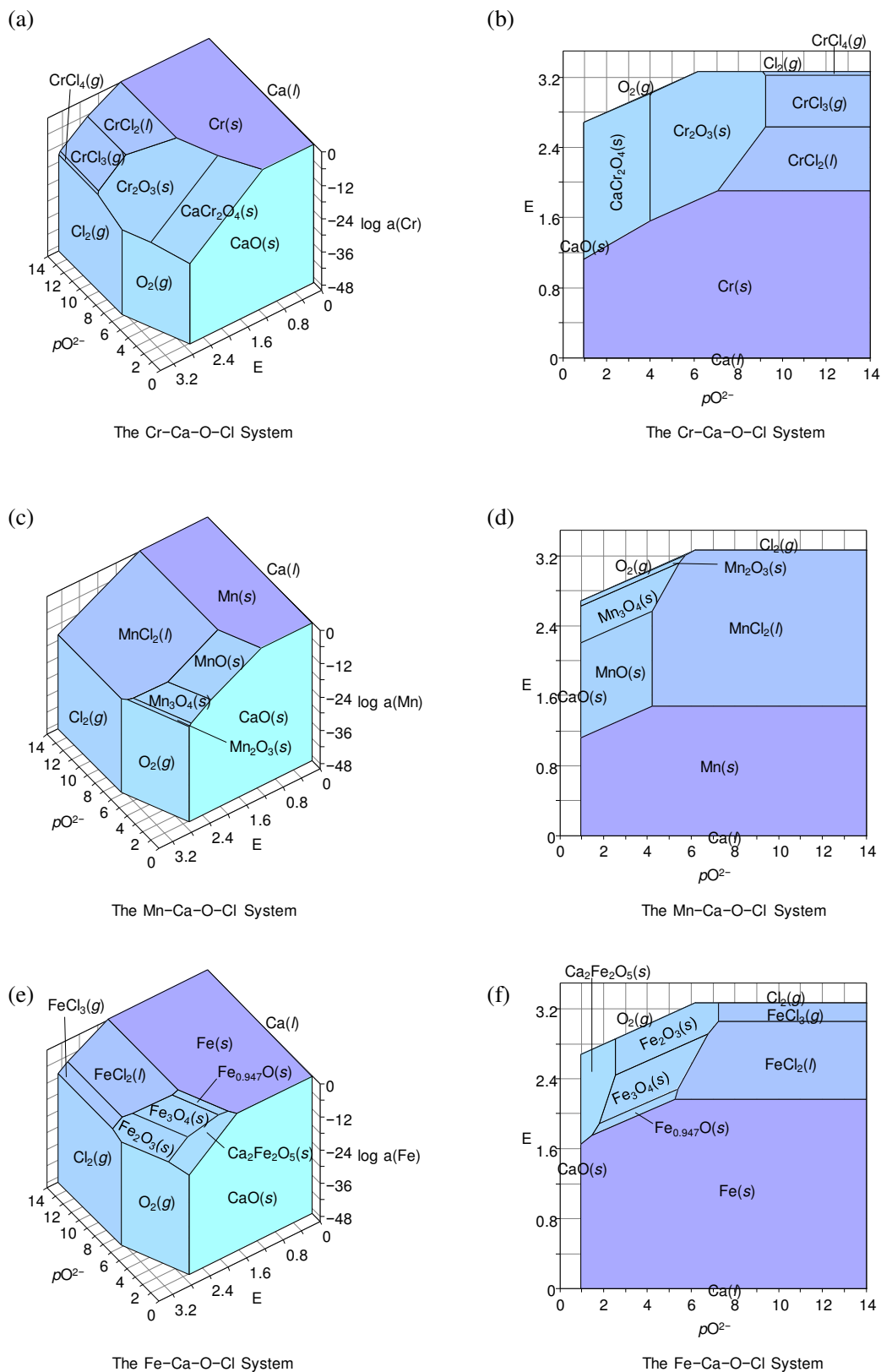


Figure A-11 Potential- pO^{2-} diagrams (a) with $\log a(\text{Cr})$, (b) projected figure for Cr-Ca-O-Cl system, (c) with $\log a(\text{Mn})$, (d) projected figure for Mn-Ca-O-Cl system, and (e) with $\log a(\text{Fe})$, (f) projected figure for Fe-Ca-O-Cl system in molten CaCl_2 at 1123 K.

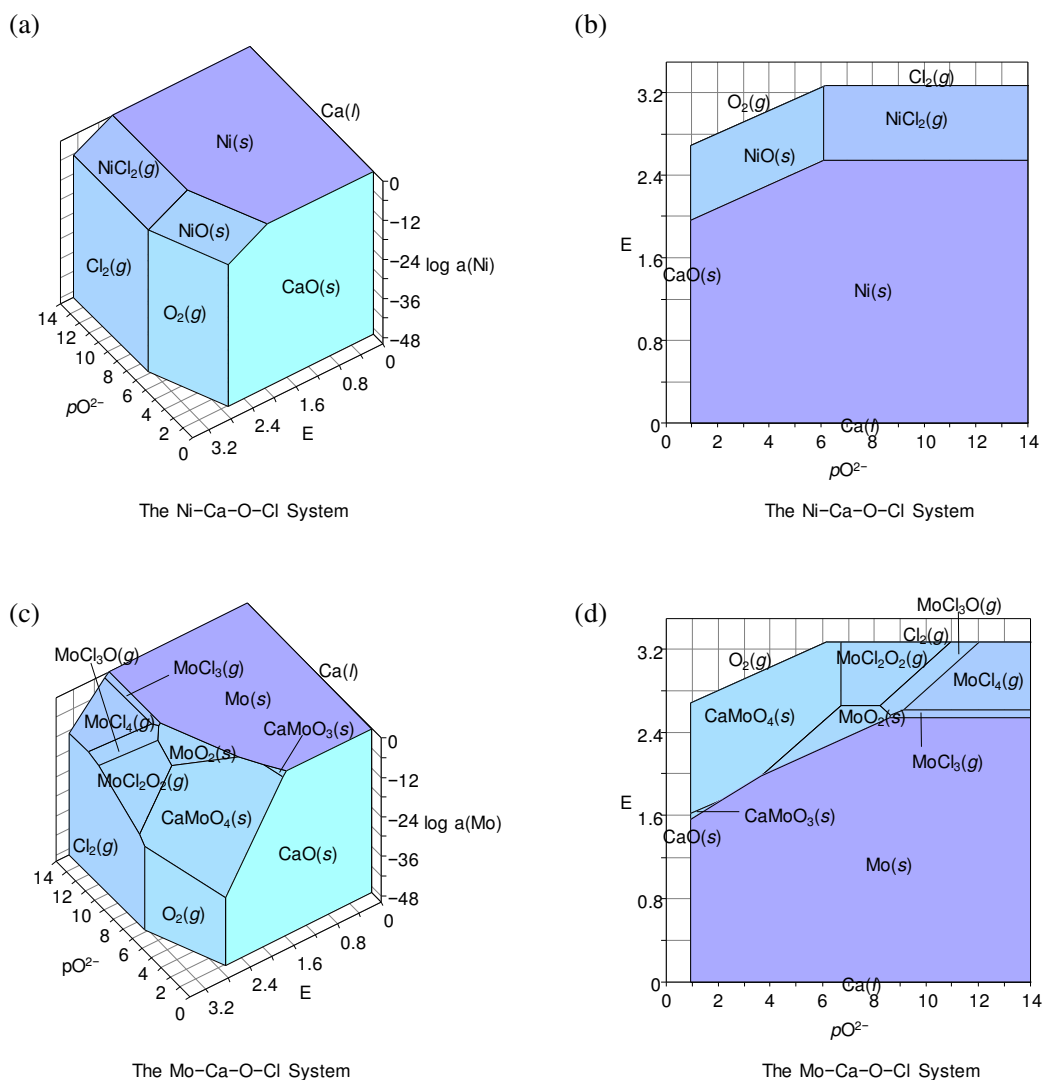


Figure A-12 Potential- pO^{2-} diagrams (a) with $\log a(\text{Ni})$, (b) projected figure for Ni-Ca-O-Cl system, and (c) with $\log a(\text{Mo})$, (d) projected figure for Mo-Ca-O-Cl system in molten CaCl_2 at 1123 K.

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Yumi Katasho