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# Space for Sustainability Award

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# **Eco-Friendly Production of Titanium and Lunar Oxygen**

Titanium is an **essential** metal for all of ESA's most ambitious space missions due to its low density, chemical resistance, and high strength. Despite its abundance, titanium extraction remains **challenging**, **expensive**, and **environmentally harmful**. With Europe relying heavily on titanium exports from Russia, an eco-friendly *and* European production method is urgently needed. The FFC process, which can utilize green electricity from sustainable sources to split titanium oxides into titanium and oxygen, offers a promising alternative. It also aligns with ESA lunar In-Situ Resource Utilization (ISRU) efforts for a sustainable exploration of space, having been used to extract nearly 100% of oxygen from the metal oxides in lunar regolith. To be commercially successful, the FFC process however requires a new technological leap. Inspired by a more than a century-old liquid cathode technology, this paper presents a **newly developed approach** to transform the FFC process into a **continuous and resource-efficient method** to ecologically produce **high-quality titanium** for Europe's space industry.

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# **Contents**



# <span id="page-2-0"></span>**1 The role of titanium in the space industry**

Titanium has been an essential raw product for the space industry ever since. <sup>1</sup> The reason is found in the unique properties of the transition metal. Compared to stainless steel, titanium has a 20 $\%^2$ greater specific strength (76 kNm kg<sup>-1)3</sup>, all while having a 40 % lower density. $^{\rm 4}$  Titanium's low thermal conductivity (22 Wm<sup>-1</sup>K<sup>-1</sup>)<sup>5</sup> supports applications in both high and low temperature environments, as found in rocket engines $6$  or cryogenic propellent tanks.<sup>7</sup> This is complemented by a high chemical resistance, even against strongly corrosive propellants like hydrazine. <sup>8</sup>–<sup>11</sup> The list of prestigious ESA missions utilizing titanium is long7,12–<sup>16</sup> , and its use cases are diverse (**Figure 1**). While Titanium is ubiquitously present in modern spacecraft, it comes with an enormous price tag for the European space sector, regarding economic, environmental, and strategic costs.



Figure 1 Examples of prestigious ESA missions relying on titanium metal. Mission patches downloaded from<sup>17</sup>.

# <span id="page-2-1"></span>**1.1 High titanium cost despite its abundance**

Titanium tanks are considered one of the costliest items in a spacecraft's propulsion system.<sup>18</sup> Contrary to what the high cost suggests, titanium is the ninth most abundant element in the earth's crust, being almost a hundred times more abundant than copper and only around ten times less common than iron.<sup>19,20</sup> Commercially viable feedstocks are found in the forms of ilmenite (FeTiO<sub>3</sub>) and rutile (TiO<sub>2</sub>).  $^{21-23}$  The extraction of titanium from these minerals is however extremely challenging, given the extraordinarily high chemical affinity between titanium and oxygen. $24$  The required energy to produce a single kilogram of titanium is estimated to be 50 kWh – 80 kWh<sup>25–27</sup>, which is roughly *one order of magnitude* greater than what is required for the same mass of crude steel.<sup>28</sup> Consequently, the price of a kilogram of titanium is around *20 times* greater than the price of a kilogram of steel, averaging around 10  $\bm{\epsilon}$  per kilogram of titanium. $^{29}$ 

# <span id="page-2-2"></span>**1.2 The state-of-the-art titanium production is environmentally concerning**

Titanium is produced on an industrial scale via the multi-step Kroll process. It requires TiO<sub>2</sub> enriched ores which are treated with hazardous chlorine gas  $(Cl<sub>2</sub>)$  and carbon (C) to form TiCl<sub>4</sub> and CO at

elevated temperatures (750 °C – 1000 °C). The TiCl<sub>4</sub> must then be purified by energy-intensive distillation steps and is subsequently reduced to titanium metal upon reaction with molten magnesium at temperatures between 800 °C – 900 °C.<sup>21,22</sup> The reaction product is a low-density and low-quality porous titanium sponge, which sticks to the reactor walls, rendering a continuous operation impossible. Subsequent purification steps are responsible for about 70 % of the total energy consumed in the process.<sup>30</sup>

The Kroll process is highly environmentally concerning. From the resource extraction to the metal product, a single kilogram of titanium is associated with 35 kg of  $CO<sub>2</sub>$  equivalents. This is **fifteen times** more than what is associated with a kilogram of steel. <sup>31</sup> Chlorine gas, being used for the formation of the highly toxic TiCl<sub>4</sub> intermediate<sup>32</sup>, poses a major hazard for humans and water organisms with long-lasting effects.<sup>33</sup> Its corrosive nature is associated with frequent maintenance and replacement of parts. Additionally, the washing of the titanium sponge with acids (HCl, HNO<sub>3</sub> or  $H<sub>2</sub>SO<sub>4</sub>$ ) creates large amounts of acidic waste (50 000 tons yearly in the United States alone<sup>34</sup>), possibly containing hazardous concentrations of chromium, selenium, and lead. Some of those waste streams are known to end up injected into deep wells or simply in rivers and seawater. 34,35

#### <span id="page-3-0"></span>**1.3 Europe's lack of titanium production capabilities is a strategic weak spot**

Currently, the European Union does not possess *any* significant titanium production capabilities and is hence strongly dependent on metal imports for its aerospace industry, which consumes two-thirds of the total imported titanium. As of October 2023, the EU imported titanium worth 308 Mio. € from the Russian Federation, its most important titanium trading partner. <sup>36</sup> This titanium is mostly obtained from the worldwide largest and vertically integrated producer of titanium, VSMPO-Avisma (20 % - 30 % global market share<sup>37</sup>), being owned to 25 % by Rostec, a Russian state-owned defence conglomerate. Due to the strong resource dependence and with respect towards its own economy, titanium is not subjected by EU sanctions.<sup>38</sup> Hence, *European countries indirectly finance the Russian war efforts*. With the European arms industry also requiring titanium imports for fighter jets, missiles, and submarines, being dependent on Russian supplies is a strategic weak spot. Within Ukraine, Europe possesses major titanium ore reserves, however it is unlikely that titanium production via the Kroll process will be largely adopted within Europe, given the major environmental and safety hazards. A new, environmentally friendly method of titanium production is thus direly needed to support the strategic independence of European countries.

# <span id="page-4-0"></span>**2 Failing to achieve eco-friendly titanium**

#### <span id="page-4-1"></span>**2.1 Previous attempts: The FFC Cambridge process**

In the early 2000 **C**hen, **F**ray and **F**arthing developed a novel process to produce titanium electrochemically.<sup>39</sup> In this so-called **FFC Cambridge**, or short, **FFC** process, TiO<sub>2</sub> is sintered into porous electrodes and directly turned into titanium powder by means of electrolysis in a molten CaCl<sub>2</sub> electrolyte at moderate temperatures (800 °C to 1000 °C). The process gained a lot of attention, as it could also be applied to a wide range of other metal oxide. <sup>40</sup> The FFC process was disruptive, as titanium production via this one-step process is drastically simplified. Green electricity can be used for the electrolysis and with further technical advancements on the anode side<sup>41</sup>, the only byproduct of the reaction is oxygen gas according to TiO<sub>2</sub>  $\rightarrow$  Ti + O<sub>2</sub>. Moreover, a kilogram of titanium produced via the FFC process only requires around 33 kWh of energy, *which cuts the energy requirements of the established Kroll process in half*. 26,27

#### <span id="page-4-2"></span>**2.2 Failed commercialization efforts**

Metalysis, a UK-based venture company, tried to commercialize this process and started the development of large-scale electrolytic cells to produce low-cost titanium beginning in 2002.11,42 The Cambridge University spinout rose around £ 94,000,000 of funding over several rounds. Despite this significant financial support, the company went into administration in 2018. <sup>43</sup> Major challenges in scale-up and high research and development cost are possible reasons behind the lack of economic success. The batch-type processing requires time- and money-intensive maintenance after every run, given the corrosive nature of molten salts and high-temperature oxidizing environments. A new technological leap is hence strongly needed to make this technology economically attractive again.

# <span id="page-4-3"></span>**3 Strategic overlap: ISRU and titanium production**

In 2020, Lomax et al. conducted a groundbreaking study partially funded by ESA, proving that the FFC process can be used to access the vast amounts of oxygen (40 wt.% - 45 wt.% $44$ ) stored within the metal oxides (termed  $M_xO_y$ ) which constitute lunar regolith.<sup>45</sup> This approach focuses on the oxygen, which was previously only a byproduct of the reaction 2  $M_xO_y \rightarrow 2x M + y O_2$ . Astonishingly, they showed that almost 100 % of oxygen could be extracted, which means that an astronaut would only need to process around 2 kg of regolith per day to create enough oxygen for his daily consumption.<sup>46</sup> In stark contrast to polar water ice, another potential source of lunar oxygen, this technology is not limited to permanently shadowed regions, which complicate mission architectures given their lack of sunlight, extreme temperatures and the missing data about the actual water quantities.<sup>47,48</sup>

Any advancements in the FFC process are directly expected to be transferable to the oxygen extraction from lunar regolith and would strongly support ESA's ISRU (In-Situ Resource Utilization) efforts. Major players in the space sector (ESA<sup>49</sup>, NASA<sup>50</sup>, CNSA<sup>51</sup>, JAXA<sup>52</sup>, ISRO<sup>53</sup>, Blue Origin<sup>54</sup>) acknowledge the key role of lunar regolith oxygen extraction by supporting related research, as it has the game changing potential of offering an in-space refuelling service. This is expected to significantly lower the number of necessary rocket launches, thereby reducing pollution on earth and in the critical top layers of the atmosphere<sup>55,56</sup>, while also reducing debris caused by spent stages in low earth orbit, which itself is a limited resource for space exploration. <sup>57</sup> The utilization of lunar regolith would hence not only benefit a sustainable (meaning long-term) human presence on the moon, but also a sustainable (meaning resourceful and planetary friendly) mission architecture.

# <span id="page-5-0"></span>**4 Application of a liquid zinc cathode in the FFC process**

# <span id="page-5-1"></span>**4.1 Inspiration from a well-established process**

The FFC process has a game changing potential for both terrestrial and lunar applications, but the fact that it cannot be operated continuously necessitates time and energy intensive cooldown and heating phases, as well as cumbersome maintenance, which is detrimental for either of the two usecases. To tackle this decisive challenge, the idea proposed in this paper is strongly inspired by the terrestrial aluminium production via the Háll-Heroult process, which is the 135-year-old, well established method globally used to produce aluminium. $^{58}$  In this process, alumina (Al<sub>2</sub>O<sub>3</sub>) is reduced to metallic aluminium via means of molten salt electrolysis at 950 °C – 1000 °C. The reduced liquid aluminium (melting point: 660 °C<sup>59</sup> ) sinks to the bottom of the crucible, where it then acts as **a**   ${\sf liquid\ cathode}$  and where it is eventually recovered by an aluminium outlet. $^{60}$  The addition of Al $_2$ O $_3$ feedstock and the removal of aluminium product can occur continuously, which is a decisive advantage, allowing the process to be profitable on large scales.

#### <span id="page-5-2"></span>**4.2 Liquid zinc cathode for titanium and oxygen extraction**

Contrary to the Hall-Héroult process, titanium itself cannot be used as a liquid cathode in a FFC related process given its high melting point of 1668 °C. <sup>61</sup> Instead, other liquid metals can be used, which will have to be removed from the titanium product at a later stage. While this approach appears exotic, liquid cathodes are a *hot topic* within the research community, given the large number of recent publications.<sup>62–76</sup> **Zinc metal**, given its affordable cost<sup>77</sup>, high density (7.14 g cm<sup>-3</sup>)<sup>78</sup>, intermediate reactivity<sup>78</sup> and medium redox potential (-0.762 V vs. Standard Hydrogen Electrode)<sup>79</sup> fulfils the most important selection criteria. The following comparison (**Figure 2**) amplifies the vast



**Figure 2** Process overview for the standard FFC process using a solid cathode and a pelletized metal oxide (left) and the proposed novel process using a liquid zinc cathode and metal oxide powder (right).

advantages of using a liquid metal cathode in contrast to the standard FFC process.

**(1)** Using a fine oxide powder as the starting material is generally beneficial, as it increases the reaction kinetics (speed of the reaction), and as it reduces process complexity. Both TiO<sub>2</sub> and regolith powders have been successfully used in the standard FFC process, but as the powder is placed on top of a solid cathode, a significant number of metallic particles fall off of the electrode, being lost at the bottom of the reactor, as previously reported.<sup>45,80</sup> Also, the metal recovery in powder form necessitates washing steps, which inevitably lead to a loss of CaCl<sub>2</sub> and lower the recyclability of the process. A workaround was found in the use of a more self-coherent sintered metal oxide pellet, which however necessitates a sintering step at temperatures above 1000 °C, increasing both energy cost and process complexity. In the novel proposed liquid cathode concept (Figure 2 on the right), the fine oxide powder *must* sink towards the bottom of the reactor, where it meets the interface between the molten salt electrolyte and the liquid zinc cathode. This ensures that no product is lost.

**(2)** The reduction of the metal cations happens at the cathode. Reduced metallic species in the regular FFC process might fuse to the stainless-steel solid cathode, as observed during experiments with regolith simulants conducted at ESA/ESTEC's ISRU facility.<sup>81</sup> This leads to a labourintensive and low-yield product recovery. On a liquid metal cathode, reduced species are collected *within* the cathode and can simply be separated by built-in zinc recycling steps (Figure 3, to be discussed).

**(3)** Oxide ions are in both cases oxidized to oxygen, which is **(4)** recovered from the system in an inert and recyclable carrier gas. While oxygen evolving anodes have been tested in this exact use case, they require further development to achieve a higher stability. $^{41,82}$ 



**Figure 3** Recovery and purification of the liquid zinc cathode after electrolysis for a closed loop operation.

At the end of the electrolysis, the standard FFC cell is cooled down, opened and the metal cumbersomely recovered. The use of the liquid zinc cathode however allows to add a separate, inline process, in a way that has not been described by literature before (**Figure 3**). After electrolysis **(1)** the liquid zinc cathode and the reduced metallic species (**M**) contained within are transferred **(2)** into a separate chamber. Given the extraordinarily low vapour pressure of zinc, moderate vacuum distillation conditions (15 mbar, 600 °C)<sup>83</sup> are sufficient to separate the zinc metal from the won titanium or lunar metals (incl. Si, Al, Ca, Mg, Fe, Ti). The zinc vapours are resublimed onto a cold finger **(3)**, which can re-release the zinc upon reheating. Recovered zinc can then be added together with metal oxide feedstock upon the start of the next electrolysis cycle. This process would not require cooldown procedures, would operate with the simplest possible feedstock, and could be run without intervention.

#### <span id="page-7-0"></span>**4.3 Risks**

The presented technology is still at the proof-of-concept stage, resulting in a low technology readiness level of 3.<sup>84</sup> Investments from the private European space sector towards further technological development are hence inherently risky, also since previous commercialisation attempts failed.<sup>85</sup> Although energy intensive and polluting, the well-established Kroll process for titanium production is dominating the market with its massive economies of scale and increases the barriers to enter this market.<sup>86</sup> Especially a lunar application of this technology will increase technological requirements, given the challenging lunar conditions. Reduced gravity levels are expected to influence the reaction kinetics, as  $O<sub>2</sub>$  gas bubbles will have a longer residence time on the active electrochemical surface area, blocking further reactions.<sup>87</sup> The harsh vacuum and the need to keep the resource cycle closed additionally increase process complexity, besides the known hazards of working with lunar dust, high levels of radiation, and lunar nights. $^\mathrm{88}$ 

# <span id="page-8-0"></span>**4.4 Potential benefits and alignment with sustainability goals**

With its Agenda 2025, ESA committed "to the fullest" (p. 13) to the Paris Agreement and the European Green Deal, aiming to become "a model for the space community and beyond" (p. 13).<sup>89</sup> In response to these commitments, the agency implemented corporate social responsibility principles towards the environment, exemplary leadership in the space community, and society<sup>90</sup>, which actively support the United Nations sustainable development goals (SDG).<sup>91,92</sup> By advancing and financing research to potentially replace the environmentally concerning Kroll process with the eco-friendly method presented herein, ESA would contribute towards eight SDGs at the same time (**Figure 4**).



**Figure 4** The eight United Nations Sustainable Development Goals supported by the proposed technology.<sup>91</sup> Eco-friendly titanium would drastically reduce the environmental impact of ESA's space hardware (**SDG13**). The proposed process, free from toxic chemicals and hazardous wastewater, would benefit public health (**SDG3**) by protecting the water cycle (**SDG14**, **SDG6**). By loosening political dependencies on Russia and by decreasing financial support for the Russian arms industry, European countries could play an increased role in peace mitigations, delivering substantial societal benefits (**SDG16**). Europe could set a global example in the space community by pioneering a new industrial process (**SDG9**) that ensures responsible production within a closed loop (**SDG12**). This innovative process could also be utilized to produce oxygen on the lunar surface, fostering a sustainable lunar community, and reducing the number of launches from Earth (**SDG11**).

# <span id="page-8-1"></span>**5 Conclusion**

Considering the clear benefits of the proposed ecological titanium production method and the promise of its transformative potential for lunar ISRU, the proposed technology blends in exactly with ESA's sustainability ambitions. While the investment risks for the private sector are considerable, ESA is uniquely positioned to drive technological innovation. By leveraging a century-old, proven technology in the field of liquid cathodes alongside the newest scientific findings, this technology promises to strengthen the European economy and advance its ambitious sustainability goals, leading the way into a greener, more sustainable future for European space exploration.

### <span id="page-9-0"></span>**6 References**

- 1. NASA History Office NHWDC. NASA Historical Reference Collection: Apollo Spacecraft.
- 2. Harvey DP. *Engineering Properties of Steels*. American Society for Metals; 1982.
- 3. Boyer R, Welsch G, Collings EW. *Materials Properties Handbook: Titanium Alloys*. ASM International; 1994.
- 4. Greenwood NN, A. Earnshaw. *Chemie Der Elemente*. 1st ed.; 1988.
- 5. James AM, Lord MP. *Macmillan's Chemical and Physical Data, Macmillan, London, UK, 1992*. Macmillan; 1992.
- 6. Rocketdyne Propulsion & Power. Space Shuttle Main Engine Orientation. *Boeing*. Published online 1998. Accessed June 11, 2024. http://www.lpre.de/p\_and\_w/SSME/SSME\_PRESENTATION.pdf
- 7. ESA. Hera Propulsion Module. Published 2023. Accessed May 30, 2024. https://www.esa.int/ESA\_Multimedia/Images/2023/08/Hera\_Propulsion\_Module
- 8. Sarraf M, Rezvani Ghomi E, Alipour S, Ramakrishna S, Liana Sukiman N. A state-of-the-art review of the fabrication and characteristics of titanium and its alloys for biomedical applications. *Biodes Manuf*. 2022;5(2). doi:10.1007/s42242-021-00170-3
- 9. Veiga C, Davim JP, Loureiro AJR. Properties and applications of titanium alloys: A brief review. *Reviews on Advanced Materials Science*. 2012;32(2).
- 10. Ikuhiro INAGAKI, Yoshihisa SHIRAI, Tsutomu TAKECHI, Nozomu ARIYASU. Application and Features of Titanium for the Aerospace Industry. *NIPPON STEEL & SUMITOMO METAL* . 2014;106.
- 11. Takeda O, Ouchi T, Okabe TH. Recent Progress in Titanium Extraction and Recycling. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*. 2020;51(4). doi:10.1007/s11663-020-01898-6
- 12. ESA. JUICE BEGINS TO TAKE SHAPE. Published October 23, 2019. Accessed May 30, 2024. https://sci.esa.int/web/juice/-/-5-juice-begins-to-takeshape
- 13. Berthe P. *Orion European Service Module (ESM) Development, Integration and Qualification Status*.; 2017. Accessed May 30, 2024. https://ntrs.nasa.gov/api/citations/20170009574/downloads/20170009574.pdf
- 14. Poulakis P. Overview and development status of the Exomars rover mobility subsystem. *ESA*. Published online 2015. Accessed May 30, 2024. https://robotics.estec.esa.int/ASTRA/Astra2015/Papers/Session%201A/96038\_Poulakis.pdf
- 15. NASA. Key Elements of James Webb Space Telescope Complete Testing at Marshall. NASA. Published November 19, 2013. Accessed May 30, 2024. https://www.nasa.gov/missions/webb/key-elements-of-james-webb-space-telescope-complete-testing-at-marshall/
- 16. Merino J. Ariane 6 Tanks & Structures for the new European Launcher. In: *Deutscher Luft- Und Raumfahrtkongress*. ; 2017. Accessed June 3, 2024. https://www.dglr.de/publikationen/2017/450255.pdf
- 17. ESA. ESA Mission Patches. Accessed June 4, 2024. https://brand.esa.int/assets/esa-mission-patches/
- 18. ESA. Friction Stir Welded Low Cost Propellant Tank. Published 2017. Accessed June 3, 2024. https://www.esa.int/Enabling\_Support/Space\_Engineering\_Technology/Shaping\_the\_Future/Friction\_Stir\_Welded\_Low\_Cost\_Propellant\_Tank
- 19. Zhang W, Zhu Z, Cheng CY. A literature review of titanium metallurgical processes. *Hydrometallurgy*. 2011;108(3-4). doi:10.1016/j.hydromet.2011.04.005
- 20. Haynes WM, Lide DR, Bruno TJ, eds. *CRC Handbook of Chemistry and Physics*. CRC Press; 2016. doi:10.1201/9781315380476
- 21. Peters M, Leyens C. *Titanium and Titanium Alloys: Fundamentals and Applications*. Vol 1.; 2003.
- 22. Tapiwa David Mutava. *Characterisation of a Titanium Precursor Salt and Study of Some of the Treatment Steps Used for the Extraction Process*. dissertation. University of the Witwatersrand; 2009.
- 23. Bundesanstalt für Geowissenschaften und Rohstoff. *Titan: Rohstoffwirtschaftliche Steckbriefe*.; 2014. Accessed February 19, 2024. https://www.deutsche-rohstoffagentur.de/DE/Themen/Min\_rohstoffe/Downloads/rohstoffsteckbrief\_ti.pdf?\_\_blob=publicationFile&v=6
- 24. Seetharaman S, McLean A, Guthrie R, Sridhar S. *Treatise on Process Metallurgy*. Vol 1.; 2013. doi:10.1016/C2010-0-66691-0
- 25. Zwicker U. *Titan Und Titanlegierungen*. Springer Berlin Heidelberg; 1974. doi:10.1007/978-3-642-80587-5
- 26. Hu D, Dolganov A, Ma M, Bhattacharya B, Bishop MT, Chen GZ. Development of the Fray-Farthing-Chen Cambridge Process: Towards the Sustainable Production of Titanium and Its Alloys. *JOM*. 2018;70(2):129-137. doi:10.1007/s11837-017-2664-4
- 27. Reddy RG, Shinde PS, Liu A. Review—The Emerging Technologies for Producing Low-Cost Titanium. *J Electrochem Soc*. 2021;168(4):042502. doi:10.1149/1945-7111/abe50d
- 28. Van Wees FGH, Over JA, Van Buuren JE, Ronde PMB. *Energyconsumption for Steel Production*.; 1986.
- 29. U.S. Department of the Interior. Mineral Commodity Summaries 2020. *US Geological Survey*. Published online 2020. Accessed June 11, 2024. https://pubs.usgs.gov/periodicals/mcs2020/mcs2020.pdf
- 30. Kohli R. *Production of Titanium from Ilmenite: A Review*.; 1981. doi:10.2172/5267009



- 46. K. Ewert M, Stromgren C. Astronaut Mass Balance for Long Duration Missions. In: *49th International Conference on Environmental Systems*. ; 2019. Accessed June 4, 2024. https://ttu-ir.tdl.org/server/api/core/bitstreams/2f4c786b-0063-4418-8722-e32f1b5d7158/content
- 47. Brown HM, Boyd AK, Denevi BW, et al. Resource potential of lunar permanently shadowed regions. *Icarus*. 2022;377:114874. doi:10.1016/j.icarus.2021.114874
- 48. Bickel VT, Moseley B, Lopez-Francos I, Shirley M. Peering into lunar permanently shadowed regions with deep learning. *Nat Commun*. 2021;12(1):5607. doi:10.1038/s41467-021-25882-z
- 49. ESA. Turning Moon dust into oxygen. Published November 27, 2020. Accessed June 4, 2024. https://www.esa.int/Science\_Exploration/Human\_and\_Robotic\_Exploration/Turning\_Moon\_dust\_into\_oxygen
- 50. NASA. NASA Successfully Extracts Oxygen from Lunar Soil Simulant. Published April 25, 2023. Accessed June 4, 2024. https://www.nasa.gov/centers-and-facilities/johnson/nasa-successfully-extracts-oxygen-from-lunar-soil-simulant/
- 51. Shi H, Li P, Yang Z, et al. Extracting Oxygen from Chang'e-5 Lunar Regolith Simulants. *ACS Sustain Chem Eng*. 2022;10(41):13661-13668. doi:10.1021/acssuschemeng.2c03545
- 52. Yuta Suzuki. *Electrochemical Processing in Molten Salt for In-Situ Resource Utilization*. Kyoto University; 2021. Accessed June 4, 2024. https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwjwo6\_7 cGGAxVp7bsIHcSbDm0QFnoECBAQAQ&url=https%3A%2F%2Fdoshisha.repo.nii.ac.jp%2Frecord%2F28188%2Ffiles%2Fzk1163.pdf&usg=AOvV aw1ROo\_lU0HH-1z4-UiMNwye&opi=89978449
- 53. ISRO. Respond Basket 2022. Published online March 8, 2022. Accessed June 4, 2024. https://www.isro.gov.in/media\_isro/pdf/programme/respond\_basket\_2022.pdf
- 54. Blue Origin. Blue Alchemist Technology Powers Our Lunar Future. Published February 10, 2023. Accessed June 4, 2024. https://www.blueorigin.com/news/blue-alchemist-powers-our-lunar-future
- 55. David Webb. *The Environmental Effects of Space Tourism*. 1st ed. Taylor & Francis; 2024. Accessed June 4, 2024. https://www.taylorfrancis.com/chapters/edit/10.4324/9781032617961-8/environmental-effects-space-tourism-david-webb
- 56. Kokkinakis IW, Drikakis D. Atmospheric pollution from rockets. *Physics of Fluids*. 2022;34(5). doi:10.1063/5.0090017
- 57. Page J, Besco L. Dispossession through collision: low-Earth orbit and planetary sustainability. *Territ Politic Gov*. 2023;11(7):1501-1518.

doi:10.1080/21622671.2021.1903543

58. Lorentsen OA. 125 years of the Hall-Héroult Process-What Made It a Success? In: *Molten Salts Chemistry and Technology*. Vol 9781118448731. ; 2014. doi:10.1002/9781118448847.ch1k

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- 59. Foteinopoulos P, Papacharalampopoulos A, Stavropoulos P. On thermal modeling of Additive Manufacturing processes. *CIRP J Manuf Sci Technol*. 2018;20. doi:10.1016/j.cirpj.2017.09.007
- 60. Brough D, Jouhara H. The aluminium industry: A review on state-of-the-art technologies, environmental impacts and possibilities for waste heat recovery. *International Journal of Thermofluids*. 2020;1-2. doi:10.1016/j.ijft.2019.100007
- 61. Merck Sharp & Dohme Corp. *Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals*. 15th ed. Royal Society of Chemistry; 2013.
- 62. Jiao H, Wang J, Zhang L, Zhang K, Jiao S. Electrochemically depositing titanium(3+) ions at liquid tin in a NaCl–KCl melt. *RSC Adv*. 2015;5(76):62235-62240. doi:10.1039/C5RA08909C
- 63. Kadowaki H, Katasho Y, Yasuda K, Nohira T. Electrolytic Reduction of Solid Al2O3 to Liquid Al in Molten CaCl2. *J Electrochem Soc*. 2018;165(2):D83-D89. doi:10.1149/2.1191802jes
- 64. Jiao S qiang, Jiao H dong, Song W li, Wang M yong, Tu J guo. A review on liquid metals as cathodes for molten salt/oxide electrolysis. *International Journal of Minerals, Metallurgy and Materials*. 2020;27(12). doi:10.1007/s12613-020-1971-x
- 65. Yasuda K, Shimao T, Hagiwara R, Homma T, Nohira T. Electrolytic Production of Silicon Using Liquid Zinc Alloy in Molten CaCl 2 . *J Electrochem Soc*. 2017;164(8). doi:10.1149/2.0121708jes
- 66. Dai W, Qin B, Liu Y, Yan H, Ma W. Electrolysis of rich Titanium Slag in Molten CaCl2 with a Liquid Zn Cathode. *Int J Electrochem Sci*. 2020;15(11). doi:10.20964/2020.11.32
- 67. Iizuka M, Uozumi K, Inoue T, Iwai T, Shirai O, Arai Y. Behavior of plutonium and americium at liquid cadmium cathode in molten LiCl–KCl electrolyte. *Journal of Nuclear Materials*. 2001;299(1):32-42. doi:10.1016/S0022-3115(01)00667-5
- 68. Telgerafchi AE, Rutherford M, Espinosa G, et al. Magnesium production by molten salt electrolysis with liquid tin cathode and multiple effect distillation. *Front Chem*. 2023;11. doi:10.3389/fchem.2023.1192202
- 69. Pu Z, Luo Y, Wang W, et al. A universal study of liquid metal cathodes for direct extraction of titanium within a closed loop. *J Clean Prod*. 2022;368. doi:10.1016/j.jclepro.2022.133135
- 70. Francois Cardarelli. Method for electrowinning of titanium metal or alloy from titanium oxide containing compound in the liquid state. Published online 2002. Accessed March 11, 2024. https://patents.google.com/patent/US7504017B2/en
- 71. Kato T, Inoue T, Iwai T, Arai Y. Separation behaviors of actinides from rare-earths in molten salt electrorefining using saturated liquid cadmium cathode. *Journal of Nuclear Materials*. 2006;357(1-3). doi:10.1016/j.jnucmat.2006.06.003
- 72. Pu Z, Jiao H, Mi Z, Wang M, Jiao S. Selective extraction of titanium from Ti-bearing slag via the enhanced depolarization effect of liquid copper cathode. *Journal of Energy Chemistry*. 2020;42. doi:10.1016/j.jechem.2019.06.004
- 73. Kado Y, Kishimoto A, Uda T. New Smelting Process for Titanium: Magnesiothermic Reduction of TiCl4 into Liquid Bi and Subsequent Refining by Vacuum Distillation. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*. 2015;46(1). doi:10.1007/s11663-014-0164-2
- 74. Lee TH, Okabe TH, Lee JY, Kim YM, Kang J. Development of a novel electrolytic process for producing high-purity magnesium metal from magnesium oxide using a liquid tin cathode. *Journal of Magnesium and Alloys*. 2021;9(5). doi:10.1016/j.jma.2021.01.004
- 75. Jeoung HJ, Lee TH, Lee JY, Yi KW, Kang J. Production of high-purity Mg metal from dolomite through novel molten salt electrolysis and vacuum distillation. *Journal of Magnesium and Alloys*. 2023;11(4). doi:10.1016/j.jma.2022.10.007
- 76. Jeoung HJ, Lee TH, Kim Y, et al. Use of various MgO resources for high-purity Mg metal production through molten salt electrolysis and vacuum distillation. *Journal of Magnesium and Alloys*. 2023;11(2):562-579. doi:10.1016/j.jma.2022.07.009
- 77. Gupta S. An econometric analysis of the world zinc market. *Empir Econ*. 1982;7(1):213-237. doi:10.1007/BF02506834
- 78. Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung. GESTIS-Stoffdatenbank Zinc. Accessed June 4, 2024. https://gestis.dguv.de/data?name=008250
- 79. Harris DC. *Lehrbuch Der Quantitativen Analyse*. 8th ed.; 2014.
- 80. Maha Vishnu DS, Sanil N, Shakila L, Sudha R, Mohandas KS, Nagarajan K. Electrochemical reduction of TiO2 powders in molten calcium chloride. *Electrochim Acta*. 2015;159:124-130. doi:10.1016/j.electacta.2015.01.105
- 81. Meurisse A, Lomax B, Selmeci Á, et al. Lower temperature electrochemical reduction of lunar regolith simulants in molten salts. *Planet Space Sci*. 2022;211:105408. doi:10.1016/j.pss.2021.105408
- 82. Chen GZ, Fray DJ. Invention and fundamentals of the FFC Cambridge Process. In: *Extractive Metallurgy of Titanium: Conventional and Recent Advances in Extraction and Production of Titanium Metal*. ; 2019. doi:10.1016/B978-0-12-817200-1.00011-9
- 83. Alcock CB, Itkin VP, Horrigan MK. Vapour Pressure Equations for the Metallic Elements: 298–2500K. *Canadian Metallurgical Quarterly*. 1984;23(3):309-313. doi:10.1179/cmq.1984.23.3.309
- 84. NASA: Catherine G. Manning. Technology Readiness Levels. Published September 27, 2023. Accessed June 5, 2024.

https://www.nasa.gov/directorates/somd/space-communications-navigation-program/technology-readiness-levels/

85. Lewis B, Cohn C. Mining company Power Resources buys Woodford-backed Metalysis. Reuters. Published June 5, 2019. Accessed February 20, 2024. https://www.reuters.com/article/idUSKCN1U01QO/

I

- 86. Cariola M. A high-potential sector: titanium metal. *Resources Policy*. 1999;25(3):151-159. doi:10.1016/S0301-4207(99)00017-3
- 87. Lomax BA, Just GH, McHugh PJ, et al. Predicting the efficiency of oxygen-evolving electrolysis on the Moon and Mars. *Nat Commun*. 2022;13(1):583. doi:10.1038/s41467-022-28147-5
- 88. Utreja LR. Lunar Environment. *Appl Mech Rev*. 1993;46(6):278-284. doi:10.1115/1.3120356
- 89. ESA. ESA AGENDA 202. Published online 2021. Accessed June 5, 2024. https://esamultimedia.esa.int/docs/ESA\_Agenda\_2025\_final.pdf
- 90. ESA. ESA Sustainability Principles. Accessed June 5, 2024. https://www.esa.int/About\_Us/Responsibility\_Sustainability/ESA\_Sustainability\_Principles
- 91. United Nations. Sustainable Development Goals. Published 2015. Accessed June 5, 2024. https://www.globalgoals.org/takeaction/?gad\_source=1&gclid=CjwKCAjwmYCzBhA6EiwAxFwfgBcLfwyWXE888h1RQgodhucsB5LaXgvIlvCWPGothU5EaLS02drfbBoCtdEQAvD\_Bw E
- 92. ESA. ESA and the Sustainable Development Goals. Accessed June 5, 2024. https://www.esa.int/Enabling\_Support/Preparing\_for\_the\_Future/Space\_for\_Earth/ESA\_and\_the\_Sustainable\_Development\_Goals