

Review

# Kenya's Mineral Landscape: A Review of the Mining Status and Potential Recovery of Strategic and Critical Metals through Hydrometallurgical and Flotation Techniques

Nelson R. Kiprono \*, Tomasz Smoliński , Marcin Rogowski, Irena Herdzyk-Koniecko , Marcin Sudlitz and Andrzej G. Chmielewski \*

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland; t.smolinski@ichtj.waw.pl (T.S.); m.rogowski@ichtj.waw.pl (M.R.); i.herdzyk@ichtj.waw.pl (I.H.-K.); m.sudlitz@ichtj.waw.pl (M.S.)

\* Correspondence: n.kiprono@ichtj.waw.pl (N.R.K.); a.chmielewski@ichtj.waw.pl (A.G.C.); Tel.: +48-50-398-3882 (N.R.K.); +48-22-504-1205 (A.G.C.)

**Abstract:** Kenya is an East African country with the third-largest economy in sub-Saharan Africa. The demand for metals and minerals continues to increase due to urbanization, population rise, and new infrastructure growth in different countries. Kenya formally confirmed the discovery of oil and various minerals in April 2013, launching itself as a new player in Africa's rapidly expanding extractive sector. This review paper highlights the mining status in Kenya and the role of hydrometallurgical and flotation processes in the recovery of deficit metals from ores and mine wastes. The nation's 2030 Vision is anticipated to benefit greatly from the proceeds from the sale of oil, gas, and valuable metals. Because Kenya was originally mapped as an agricultural region, less mineral prospecting was done in earlier times. The country's mining industry is now dominated by the manufacture of non-metallic goods, and it is largely neglected for minerals. One of the most serious problems for the mining industry in Kenya is the production of tailings that hold strategic metals. The material is already ground, which means the most energy-consuming process has been already applied, and chemical engineering processes like leaching are more feasible at this point. Hydrometallurgical and flotation recovery of valuable metals from wastes, high and low-grade ores, or tailings is essential. The resources will be preserved, which ensures sustainability in the growth of the mining industry.

**Keywords:** mining; ores; tailings; hydrometallurgy; recovery; strategic metals; critical metals; flotation



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## 1. Introduction

Mining is the practice of extracting valuable minerals or other geological materials from the Earth's crust, for economic development. These materials can be found in seams, reefs, lodes, orebodies, etc. Sustainable growth satisfies existing demands without jeopardizing the capacity of future generations to meet their needs. Justifiable development must be implemented in all human pursuits, and this requires responsible mining. It is no longer possible to extract raw materials just based on economic considerations; social and environmental factors must also be taken into account. As a result, minimal environmental effects, human health safety, full resource utilization, and waste-free mines should all be goals of good practice standards for mining and processing mineral resources [1]. Mineral-rich nations make use of these resources to shift their economy in the direction of sustainable development. Because of their abundant mineral resources, countries like South Africa, Australia, the United States, China, and Ghana, among others, are now industrialized [2]. The mining industry is anticipated to be the main engine of industrial expansion in low-income countries, particularly in Africa. These African nations include, among others, Kenya, Ghana, South Africa, Mali, and the D.R.C. (Democratic Republic of the Congo). Initiatives such as the Africa Mining Vision (AMV), a "pathway" developed by

African states themselves, place the continent's long-term and wide development goals at the center of all policy formulation related to mineral exploitation. It was started to aid in the economic transformation of Africa's mineral-rich regions [3].

Since the Industrial Revolution, the use of energy resources (primarily fossil fuels) has increased dramatically on a global scale [4]. In the coming decades, it is projected that the global energy sector will experience a continuous shift towards renewable energy alternatives [5]. With an expected rise of electricity demand of 150% from the year 2010 to 2050, renewable energy solutions, including photovoltaic power, hydroelectric power, and wind power, are going to play a significant part in satisfying future global demands [6]. The need for key metals will increase substantially as a result of the broad acceptance of technologies with low carbon footprints [5]. As millions of humans adopt contemporary ways of life, the demand for vital metals is, in fact, on the rise [7]. Still, the loss of minerals required for renewable energy technologies could make it more difficult to move from a fossil fuel-based to eco-friendly substitutes. Kenya is one of the ideal places that can contribute strategic and critical metals to the global economic chain. Therefore, this study reviews Kenya's present situation concerning strategic and crucial metals and discusses techniques for recovering them through hydrometallurgical processes. The article also, in its last section, introduces the concept of strategic and critical metal recovery using flotation techniques. Proposals and prospects for the future application of the described technologies in Kenya have also been given.

#### *Strategic and Critical Metals*

Strategic metals are resources required for vital use in times of crisis, but their acquisition is uncertain in terms of quality, quantity, and timing and any justification for their supply would require advanced planning [8]. When a metal is essential to the state's economic strategy, which includes its defense, energy, and security strategies, it is also said to be strategic. However, metal could be seen as strategic for a certain business or set of industries, including those in the automobile, renewable energy, aerospace, nuclear, ICT (Information and Communication Technologies), and electronics sectors, and so on. Each region has specific types of metal that have been determined to be crucial and strategically important for their economies. Kenya classified Ti, gas, oil, Cu, diamond, Au, Nb, gypsum, sand, and fluor spar, amongst others, as strategic and critical materials for Vision 2030 [8]. However, a region like the United Kingdom outlined Sb, Be, Cr, Au, Hf, In, Co, Ga, Ge, platinum group metals (Pt, Ir, Pd, Os, Rh, Ru, Re), REEs (Rare Earth Elements), Ta, Ti, W, Li, Mg, Ni, Nb, and V as strategic and critical materials.

Critical metals are those that are expensive, difficult to substitute for, geologically rare, prone to potential supply constraints, and required for an economically significant drive. These metals are significant due to their unique features. The possibility of supply restrictions seems to be the most important aspect of these characteristics. Unlike in the 1950s, almost every metal in the periodic table is needed currently to produce different products for society, Figure 1. A good percentage of these crucial metals were disregarded and treated as mine waste fifty to sixty years ago [9].

1		Mined in 1950s										Strategic in 2022						2																	
1	H																	2	He																
3	Li	4	Be											5	B	6	C	7	N	8	O	9	F	10	Ne										
11	Na	12	Mg											13	Al	14	Si	15	P	16	S	17	Cl	18	Ar										
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	•	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	
87	Fr	88	Ra	••	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Cn	113	Nh	114	Fl	115	Mc	116	Lv	117	Ts	118	Og	
Lanthanides series		57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu				
Actinide series		89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr				

**Figure 1.** A periodic table displaying the aspects of various types of metals and their economic status [10].

Metals such as REEs, Ge, Ta, Se, Sn, In, Ga, and Te are geologically sparse, though crucial [11]. Relatively low atomic weight La, Ce, Pr, Nd, and Pm are categorized as light REEs (LREEs) while Sm, Tm, Yb, Eu, Dy, Ho, Gd, Tb, Er, and Lu are classified as heavy REEs (HREEs) because of their high atomic weight. Since they are widespread, even though it is rare to locate them in quantities large enough to permit the production of profitable minerals, these elements are referred to as REEs [12]. Due to their occurrence in ore deposits comparable to those of lanthanides and exhibiting the same chemical properties, Y and Sc are likewise classified as REEs [13,14].

When contrasted to the other elements in the periodic table, REEs exhibit distinct magnetic, electrical, optical, luminescent, and chemical properties [15]. Considering that the majority of REEs have similar oxidation states and atomic radii, they can substitute one another in a variety of crystal lattices. Due to this substitutional capacity, numerous REE occurrences can be found in a single mineral, which leads to a widespread distribution of REEs in the Earth's crust. They can be found in a variety of mineral forms, including oxides, carbonates, phosphates, silicates, and halides. Generally, REEs are high on the priority list of essential metals in many nations where these metals are in short supply [13].

## 2. Mining Situation in Kenya

Kenya, located in the eastern part of Africa, is richly endowed with different types of mineral resources. The Kenyan government assessed its mineral potential and produced a working document in 1999, and over 400 mineral occurrences were identified. The government introduced regulations to drive this sector [16]. Vision 2030 recognizes the such industry as one of the key drivers of the country's economic development. Growth in this sphere is expected to increase the number of jobs, the income of the workers, and the country's GDP (Gross Domestic Product). The 2010 constitution created Counties and gave them the capacity to establish and carry out their development strategies. This new dispensation is forcing Counties to assess their resources and exploit them for their local development. The resources vary from County to County and are highly dependent on the topography, drainage, ecology, and climatic conditions of the County. The worldwide demand for minerals is projected to progressively rise at a mean rate of approximately

3% annually [17]. That is likely to trigger more exploration and mining activities in the resource-endowed regions of the country.

Because Kenya was originally mapped as an agricultural region, less mineral prospecting was done in earlier times. The country's mining industry is now dominated by the manufacture of non-metallic goods, and it is largely neglected for minerals. For instance, Kenya is the world's third-largest supplier of soda ash and ranks seventh in terms of fluorspar production. Additionally, Kenya formally confirmed the discovery of oil and various minerals in April 2013, launching itself as a new player in Africa's rapidly expanding extractive sector [18]. The non-renewable resources mentioned above are, regrettably, mainly found in places with high rates of poverty, ongoing droughts, instability, and long-term marginalization by the government. Conflicts between local communities, international corporations, and governmental organizations are consequently high [19].

Fe ore, Ti, and Au are amongst the metallic minerals now produced in the country. Kenya's export data show that this industry is constantly expanding. Along with industrial minerals like talc, gypsum, dolomite, and gemstones, Kenya's mineral suite also contains resources like Ag, Cu, and Zn, REEs, coal, limestone, soda ash, Mn ore, fluorspar ( $\text{CaF}_2$ ), diatomite, chromite, Nb, and silica sand. Natural fluorspar ( $\text{CaF}_2$ ), largely mined in Kenya, is typically associated with other minerals such as phosphates ( $\text{PO}_4^{3-}$ ), quartz ( $\text{SiO}_2$ ), celestite ( $\text{SrSO}_4$ ), galena ( $\text{PbS}$ ), calcite ( $\text{CaCO}_3$ ), barite ( $\text{BaSO}_4$ ), and chalcopyrite ( $\text{CuFeS}_2$ ) [20]. The most valuable REE resources in the world are also located in the coastal region (Jombo Complex) at Mrima Hills, where Cortec Mining Kenya Limited estimated that they could have an in-ground value of up to USD 62.4 billion [19,21,22]. Mrima Hill is home to a carbonatite cluster. The laterite capping resulting from the weathering of the hill's igneous constituents has economic grades of REE and Nb mineralization [23].

In terms of Counties, Turkana County has oil, gypsum, graphite, Zr, Nb, Ba, Pb, Fe, Te, Ag, Mn, Cu, and Ni ores, whereas Taita Taveta principally possesses Fe, Mn, Cu, and quartz. While Kwale County is abundant in Zn, Pb, Cu, U, Ti, REEs, Nb, and oil, Kitui County has significant amounts of Fe, coal, Cu, limestone, amethyst, and sapphire. Lamu County is rich in Ti, gas, and oil, whereas Migori County has commercially exploitable deposits of Zn, diamond, Au, Al, Fe, and Cu. Au generation in Migori and other regions is a significant driver of the nation's economic development and growth, contributing approximately USD 10.3 million/year to the country's economy [24]. Transmara and Migori districts began to mine Au in the year 1930. However, industrial mining became significant recently in the country due to the discovery of Au-bearing reefs in the Lologorien region. The local population and various enterprises that perform mining operations in the area now rely heavily on these activities as one of their main sources of income [25]. Figure 2 shows some of the minerals that have been confirmed to be available for economic purposes in Kenya.

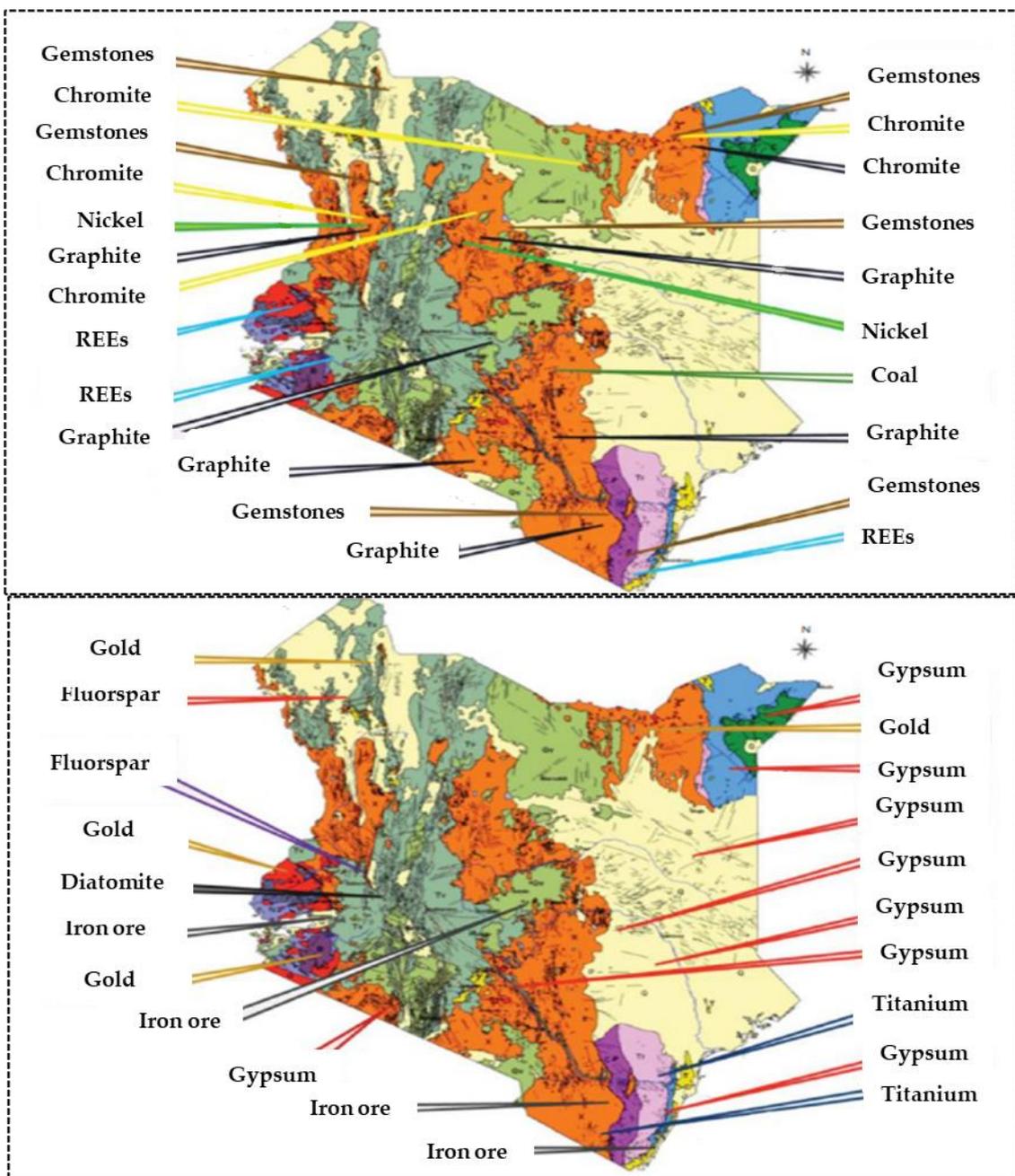


Figure 2. Maps showing mineral occurrence in Kenya [26].

For the nation to achieve the objectives of Vision 2030, the Fe and steel industry will play a significant role in the industrialization process [27]. Fe minerals are widely present in western Kenya, especially in Nyanza. Furthermore, there are untapped reserves of Fe ore in various Kenyan Counties, including Taita Taveta (Manyatta), Siaya (Samia), and Taraka (Marimanti). Although complicated, the process of making steel essentially involves melting Fe ore in a blast furnace along with coke. In some rural areas of Kenya and the neighbouring nations, the manufacturing of sponge Fe has been accomplished by smelting Fe ore using charcoal and a forced air draught from bellows made of goatskin. The majority of the ores were first crushed and sent straight to a blast furnace, especially those with 50% or more Fe without beneficiation. To increase the Fe content and get the concentrate ready for the blast furnace, the majority of extracted ores nowadays go through beneficiation [27].

Some of the platinum group metals have also been reported in Kenya. In 14 petrologically distinct spinel peridotite xenoliths found in the Marsabit volcanic zone (Kenya Rift), platinum group metals were identified [28]. However, their concentrations are very low. Marsabit's xenoliths have a total platinum group metals concentration that ranges from 14 to 32 ppb. Unfortunately, such concentrations are too low to be recovered for economic purposes.

Understanding the principles influencing element distribution in the Earth's crust is important. In particular, the role played by rocks and minerals in the uptake of certain metals from groundwaters requires comprehension of the movement and fixation of elements. Scientists have researched the compositions of several hot water springs, related minerals, rocks, and fossil bones from Kanjera and Kanam near Lake Victoria in Kenya. The location selected for the study was ideal due to the presence of volcanic hot springs and sedimentary deposits connected to Homa Mountain's carbonatite complex, which is comparatively rich in REEs [29]. The findings provided evidence of the absorption and mobility of REEs. Bicarbonate and fluoride were found to be abundant in the spring waters of both locations, and Kanjera's Zr concentration was exceedingly high. All examined rock samples had higher REE contents than chondrites. The rocks further showed higher concentrations of light REEs (Nd, Sm, La, Ce, Eu, and Gd) than heavy REEs (Tb, Yb, Lu, Ho, and Tm). The travertine specimen seemed to be moderately discoloured by Mn and/or Fe<sub>2</sub>O<sub>3</sub> or hydroxide deposits. The acid-insoluble component of the travertine (5.08% by weight) included less than 11% of each REE but more than 60% of the aggregate concentration of some elements, including Cr, Hf, and Ta. The REEs, Th, and U were generally present in fairly large quantities in the carbonate (acid-soluble) fraction. It was notable because such levels were precipitated from percolating ground water. Contrarily, the trona sample only contained detectable levels of the following elements: Ce, Sm, Sc, Cr, Eu, Co, and Th. It was concluded that groundwater-rock interaction has a significant impact on rock and mineral composition [29].

### *2.1. Environmental Impacts of Mining Activities*

Mining in Kenya and Africa at large is considered one of the main pillars of socio-economic benefits. However, the same industry is known to be amongst the main sources of pollutants. The influence of mining on environmental contamination can be both geogenic (related to parent rocks) and anthropogenic, encompassing man-made activities such as chemical use [30]. The discovery of mines and their exploitation was solely determined by the economic aspect when the exploitation of natural resources began many years ago. However, tailings production is one of the major issues facing the mining industry. Tailings encompass the remains of the fine-grained (1 to 600 µm) ground rock after the metals of value have been removed from the mined ore [31,32]. Such materials are very reactive, attributable to their minute particle size, with the variation of their chemical and physical properties depending on the ore type. Most of the tailings result during the beneficiation process.

Nearly all the heavy metals in the ores exist as compounds with sulphide in their structures. That contributes to the acid mine drainage (AMD) in the region, responsible for the death of several fish in places like Lake Victoria and the surrounding rivers. AMD is produced when sulphide-containing minerals such as pyrite are exposed to water and oxygen, where oxidation of the minerals results in the generation of hazardous H<sub>2</sub>SO<sub>4</sub> acid. AMD is one of the serious environmental challenges associated with the discharge of acidic, metal, and sulphate-containing industrial wastewater into the surroundings [33].

Additionally, wastes produced by mining activities contain elevated concentrations of metalloids and metals. The elements can be mobilized, infiltrating into the surface water and groundwater [34]. A significant fraction of such elements in industrial wastes are non-biodegradable and highly toxic. Chemical contamination occurs when the reagents added by the mineral processing industries are released. For instance, cyanide or Hg for extracting Au or H<sub>2</sub>SO<sub>4</sub> acids used in leaching Cu oxides can be supplemented under controllable

conditions but may leak into the environment if not properly handled. Alternatively, chemical pollution can occur when naturally occurring minerals are oxidized [35]. This is mainly predominant when sulphide minerals are involved while extracting Au. Other metals released during artisanal Au mining in regions like Migori and related industries include Cu, Cd, Ni, Zn, Pb, and As, all discharged into soil and water bodies [24].

Kenya is one of the countries in Africa that aims to intensify the extraction of REEs and other metals from various sources. The intricate process of mining resources such as REEs may result in negative effects on the environment and human health. The effects of mining on the environment, nevertheless, rarely receive adequate attention in the majority of developing nations. Deforestation, water contamination, soil erosion, changes in landscape structure, and the destruction of wildlife habitats are a few of the environmental effects of recovering REEs from ore. The effects of REEs are influenced by the type of rock around its deposit, the availability of additional metals or substances within the rocks, the climate, and the distance from streams and lakes to the mine.

Since agricultural land is lost due to the expansion of the mining sites, vegetation in mining areas is also destroyed during ore extraction [36]. Moreover, mine closure results in numerous wastes and the degradation of the land once minerals have been extracted to a considerable extent and the remaining ones are no longer commercially viable for extraction. Information for mitigating potentially hazardous environmental effects following the closure of mining activities and preventing particulate matter emissions from mines should be made available. This is critical, along with the responsible use and disposal of metal-bearing technology devices [36]. Furthermore, treatment of tailings and the repurposing of them will be crucial.

## 2.2. The Presence of Critical and Strategic Metals in the Mine Wastes

Valuable metals can be economically recovered from the tailings produced during mining operations. When selecting the tailings for use in an alternate application, consideration must be granted to the tailings' physical and chemical characteristics [37]. In the dominant geological circumstances within which they are found, the minerals that make up economically valuable ores are largely stable. Their chemical stability decreases when they are exposed to the atmosphere. That explains the high reactivity of tailings. Despite containing 94% of the processed ore, these wastes still contain valuable metals [38]. Thus, from the perspective of protecting the environment and preserving raw materials, continued treatment of these wastes is possible. Additionally, the material has already been pulverized, consuming the high amount of energy in the process; hence, chemical engineering procedures such as leaching become subsequently more practical at this stage [39].

Mine waste deposits are increasingly becoming dependable sources of critical and strategic metals, though some of them could be regarded as low-grade ores based on the current standards [40]. Closing the consumer cycles through the liberation of these metals from complex and dilute waste streams will become significantly viable economically [41]. Access to mine deposits is easy because they are localized at the surface without considerable overburden. The mineralogical composition of the tailings can vary depending on the ores containing the metals of interest. Discarded tailings have been found to contain significant amounts of critical metals such as Ga in bauxite residues or Ge or In in the residues of Zn ores, among others. The processing of the tailings from the ponds and waste-rock heaps of the Penouta mine in Spain led to the recovery of Ta and Nb [42]. However, the crucial influencing factors include the quantities or volumes of the critical raw materials, their concentrations, quality of tailings, and the composition of the minerals in the extractive wastes.

There have been reports of tailings in Kenyan mining industries, including the short-lived Au mine in the Migori district. Both open-cut and subsurface mining techniques were used. After that, the ore was pulverized and panned, leading to huge heaps of tailings and waste rocks. Several elements like Ti, Cr, Rb, Sr, Y, Mn, Zn, As, Au, Pb, Fe, Co, Cu, Zr, and Nb exist in various quantities in the Migori region [25,43]. Such minerals are crucial,

and they can be reprocessed for economic gain. For instance, through the application of magnetic separation methods, valuable  $\text{TiO}_2$  can be extracted from the waste [44].

Western Kenya is another region endowed with minerals such as Au, which was exploited by the British firm known as Rosterman Au Mine industries in the 1930s before they exited the site in 1952. Since the firm's exit, artisan-based miners have been extracting Au deposits from the tailings of the abandoned mines. Alluvial mining is one of the mining techniques used by artisan miners, which encompasses the excavation of the ore from the slow-moving parts of River Isiukhu [45]. The tailings and the gravel of the ore obtained are transported to appropriate locations for processing through panning or sluicing. In the majority of the mining sites, the sluiced tailings are scavenged numerous times before they are ultimately disposed of, to achieve recovery of the Au deposits lost in the previous operations [32].

### 3. Recovery of the Strategic and Critical Metals from Various Sources

The numerous minerals that are already present in Kenya can be recovered using a variety of techniques devised by academics from around the world. For the benefit of the nation, Kenyan researchers and the mining sector can adopt and improve such techniques. Compared to pyrometallurgical methods (roasting, smelting, calcining, and thermal refining of the minerals), hydrometallurgical technologies (leaching, solvent extraction, precipitation, and ion exchange amongst others) offer a greater chance of efficiently recovering very low concentrations of metals with less energy use. Pyrometallurgy has been linked to low metal recoveries, increased air pollution, and huge consumption of energy. Consequently, our review article places a strong emphasis on hydrometallurgy because it is a better alternative.

#### 3.1. Leaching

Leaching is one of the crucial steps in the recovery of metals from different materials. However, the process is non-selective; hence, there is a necessity to recover metals from the pregnant solutions using other selective methods like solvent extraction, ion exchange precipitation, etc. The reagents used in the leaching process vary. For extracting base metals such as Cu, chemicals like inorganic acids can be used [46]. These agents are commonly used with oxidants, which enhances the efficiency of the process. For precious metals such as Au, the reagents used are halogens, cyanide, and thiocyanate. Cyanide is the most excellent in the reclamation of precious metals from both secondary and mineral sources [47].

There are various types of leaching approaches, including bioleaching and chemical leaching. Bioleaching is the biological solubilization of metals from wastes and minerals. That means micro-organisms (for example, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) converting solid, insoluble metals and their compounds into extractable forms. Nonetheless, chemical leaching involves the use of bases/acids, chelating agents, surfactants, redox agents, or salts to liberate the metal from the solid phase to the aqueous phase. Both organic and inorganic acids can be utilized for chemical leaching. EDTA (Ethylenediaminetetraacetic acid) is one of the common chelating agents for various metals. However,  $\text{NaClO}$  and  $\text{H}_2\text{O}_2$  are the prominent oxidizing agents employed to improve the recovery of the metals from the solid phases [47].

Several technological methods use chemical leaching to process ores (in situ, heap, and dump leaching). The in situ approach involves the application of a lixiviant ( $\text{H}_2\text{SO}_4$ , thiosulphates, thiourea, and cyanides) which is pumped directly into the channels in the rocks or inactive mines. After some time, the resulting pregnant leach solution is pumped to the surface and then taken for post-processing for metal recovery. The technique can be used in the recovery of U and Cu [48]. Contrarily, in heap leaching, the piles are placed in the open air on a previously prepared impermeable pad (plastic, clay). The largest grains are at the base of the pile and the most pulverized at the top. The particle sizes of typical ores range from 10 to 100 mm. The leaching agent is sprinkled on the upper surface of the layer and percolates through it. An aqueous solution with dissolved metals is received

through the collecting channel [48]. Similar to this method is dump leaching, except that the ore is taken directly from the mine and stacked without crushing. The method is used for recovering Cu and precious metals and can be applied in extracting low-grade ores [49].

### 3.2. Solvent Extraction of the Common Transition Metals and Uranium

Given its capacity to cope with enormous quantities of diluted pregnant liquor of aqueous solution, solvent extraction is a widely recognized hydrometallurgical procedure. The technique is frequently used in the recovery of leached d-block, REEs, and precious metals using extractants. The extractant is an organic ligand that is intended to coordinate with the cations in a targeted manner [50]. This procedure is mostly accomplished by vigorously agitating the two immiscible media, enabling the solute(s) to be transported from one phase to the other in a controlled manner. Normally, there are two phases involved: an organic phase, having the extractant dissolved in a suitable hydrocarbon diluent; and an acidic aqueous medium, having the target metal ion(s) [51]. The pure extractant is occasionally employed as an organic solvent. However, because of its high viscosity, pure extractants are typically not used. For high product purity and large-scale manufacturing, solvent extraction is a more practical technology that has gained widespread acceptance. The above technique is incredibly practical in hydrometallurgy since it does not require specialized equipment, and it uses inexpensive chemicals to extract metals from their secondary and primary resources [52].

In recent years, there has been an evident expansion in the industrial application of Ni and Co. This may be seen in two ways: the rise of the manufacture of such metals globally, and on the other side, the presence of progressively greater quantities of different wastes containing Co and Ni [51,53–55]. These metals' unique characteristics, such as their exceptionally high melting and boiling temperatures, hardness, thermal conductivity, electrical and changing oxidation states, magnetism, and propensity for forming alloys with additional elements, make their recovery and recycling intriguing at the moment. The isolation of Ni and Co requires high precision due to their comparable physicochemical characteristics. The most important step in the process is selecting an appropriate extractant, which is typically dependent on the acidity and constitution of the leaching mixture [56]. By utilizing diverse techniques, researchers have attempted to enhance the solvent extraction approach. An efficient extractant for the separation of Ni and Co was reported to be Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid]. Cyanex 272 and D2EHPA [Di-(2-Ethyl Hexyl) phosphoric acid] can be used to separate Zn and Mn from Ni in the leach solution. According to the observations, Cyanex 272 and D2EHPA produced a superior separation of Ni and Co [56].

Kenya was ranked as the 10th highest exporter of Nb, Ta, V, and Zr ore worldwide in 2021, with USD 44.1M in exports of these metals [57]. Nb, Ta, V, and Zr ore was rated as Kenya's 29th most exported good that year. Such critical metals can be recovered through hydrometallurgical procedures. In recognition of its exceptional physicochemical properties, V—often referred to as the “vitamin of modern industry”—is used extensively in various industries. The two primary categories of V recovery methods are roasting extraction and direct extraction [58]. The extraction of  $V^{4+}$  and  $Mn^{2+}$  was explored using new technology for selectively separating and extracting them from a co-leaching mixture of roasted stone coal and pyrolusite via solvent extraction. According to the findings, 99.13% of  $V^{4+}$  was recovered using three counter-current extraction steps with 5% (*v/v*) EHEHPA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and an organic/aqueous (O/A) ratio of 1:1 under a starting aqueous pH of 2.0. With three counter-current extraction stages, 99.74% of  $Mn^{2+}$  was extracted by applying 40% (*v/v*) D2EHPA with a 60 mol% saponification effectiveness at an O/A phase ratio of 2:1 and a preliminary aqueous pH of 3.5. Following a two-stage counter-current experiment using 1 M  $H_2SO_4$  at a 2:3 O/A phase ratio,  $Mn^{2+}$  was found to be completely scrubbed off [59].

A synergistic recovery method for  $Cu^{2+}$  and  $Zn^{2+}$  ions from chloride aqueous solutions has also been developed. The selective extractant was obtained through a combination

of trioctylphosphine oxide (TOPO) and Aliquat 336. Employing 0.06 M Aliquat 336 and 0.025 M TOPO in kerosene,  $Zn^{2+}$  ions were effectively separated from  $Cu^{2+}$  ions [60]. Equivalent amounts of both phases (10 mL each) were physically mixed for 20 min during the process at a fixed temperature ( $25 \pm 2$  °C). The mass balance was then used to determine the distribution ratio ( $D$ ) of the cations measured by an atomic absorption spectrometer, Equation (1).

$$D = \frac{[Me]_{org}}{[Me]_{aq}} \quad (1)$$

Equation (2) gives the extraction percentage (%  $E$ ),

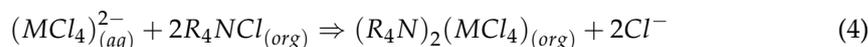
$$\% E = \frac{D}{D + 1} \times 100 \quad (2)$$

where the concentrations of the metal ions in the aqueous and organic media are  $[Me]_{aq}$  and  $[Me]_{org}$ , respectively.

$$S = \frac{D_{M1}}{D_{M2}} \quad (3)$$

Equation (3) was used to obtain the selectivity coefficient of metal  $M1$  over metal  $M2$ .

Low recovery of  $Cu^{2+}$  with TOPO was observed in the 0.1 to 2 M range. However, the extraction efficiency of  $Zn^{2+}$  and  $Cu^{2+}$  from HCl solutions with Aliquat 336 was reported to be quite high. In HCl solutions containing 0.05 M Aliquat 336, selectivity coefficients of  $Zn^{2+}$  over  $Cu^{2+}$  were very low. The extraction of  $Cu^{2+}$  and  $Zn^{2+}$  to the organic phase can be linked to results in the formation of their anionic complexes at greater chloride concentrations. The  $Cl^-$  ions' impact increases the development of recoverable anionic compounds such as  $ZnCl_3^-$ ,  $ZnCl_4^{2-}$ , and  $CuCl_4^{2-}$  species in the aqueous phase. That increases the extraction of Zn and Cu. As a result, Aliquat 336 is highly effective at removing these metal ions from the solution. This chemical functions as an anion exchanger. The reaction between the Aliquat 336 extractant ( $R_4N^+Cl$ ) and the metal can be represented as Equation (4) [60]:



The Institute of Nuclear Chemistry and Technology (INCT) in Warsaw, Poland, has also created several technological schemes for recovering strategic metals from different waste materials. The institute examined if Zn, Mn, and Mg could be separated from used Zn electrolytes selectively, Figure 3. D2EHPA diluted in n-heptane was used to extract these elements. The separation of the metallic compounds from the  $SO_4^{2-}$  mixture having 0.89 g/dm<sup>3</sup> of Mn, 15.9 g/dm<sup>3</sup> of Zn, and 24.3 g/dm<sup>3</sup> of Mg was evaluated. According to the study's findings, both for Zn and Mn, the extraction equilibrium was reached after 4 min, during which pH modulation regulated the extraction's selectivity [10].

Cu floatation tailings have substantial amounts of Cu, plus other toxic elements such as Pb, Zn, U, and Co. The regularly applied methods in the Cu mining industry often result in great losses of the deficit and valuable metals in the streams of their tailings. The formulation and implementation of hydrometallurgical advancements is a solution that is viable for higher efficiency in recovering various elements [61].

A research investigation on the extraction of Cu and other metals was performed by INCT [62]. An O/A ratio of 1:1 was used in the extraction procedure, and the extractant used comprised a combination of benzoic acid (0.5 M), the aromatic solvent toluene, and the aromatic amine p-toluidine (0.25 M).  $Cu^{2+}$  ions were removed using an aqueous sulphate solution. With the help of sodium carbonate, the aqueous phase's pH was kept between 3.6 and 3.8. Other metal ions, such as  $Ni^{2+}$  and  $Co^{2+}$ , could be separated once the Cu ions had been separated. The procedure was carried out by shaking at 25 °C in a mechanical shaker. In the majority of cases, distribution equilibrium was reached with a shaking time below 60 min. Ion separation was continued until metal ions were recovered to a degree greater

than 99%. The extraction of V, Mo, and U was studied using D2EHPA in toluene. The concentrations considered in the research were 0.3, 0.2, and 0.1 M. The extraction processes took place for 15 min under O/A ratio of 1:1. With 5% Na<sub>2</sub>CO<sub>3</sub>, the organic phase was back-extracted for 15 min. A 100% extraction from the pregnant solution was confirmed by a total transfer of Cu into the organic phase. The scholars were able to significantly speed up the analytical work using the radiotracer approach, which was a very helpful research tool. The radiotracer was essential in determining the ideal conditions that produced the highest possible recovery efficiency for Cu. The findings could be utilized as a guide when designing procedures for recovering Cu and other supporting components from flotation tailings after Cu ores have been processed, as shown in Figure 4 [62]. The scheme represents two options of hydrometallurgical process application: recovery of metals from flotation tailings or low-grade Cu ore.

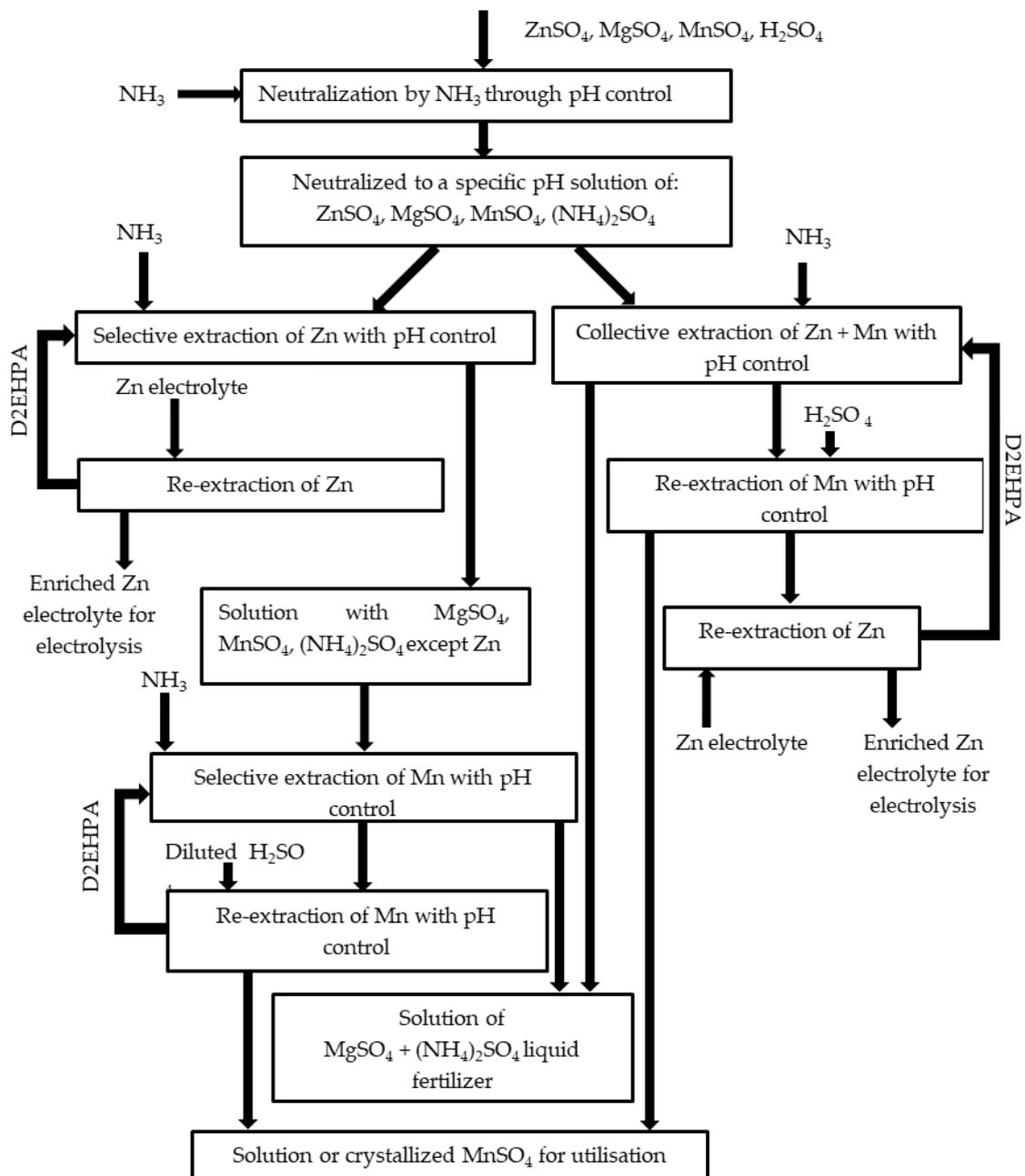
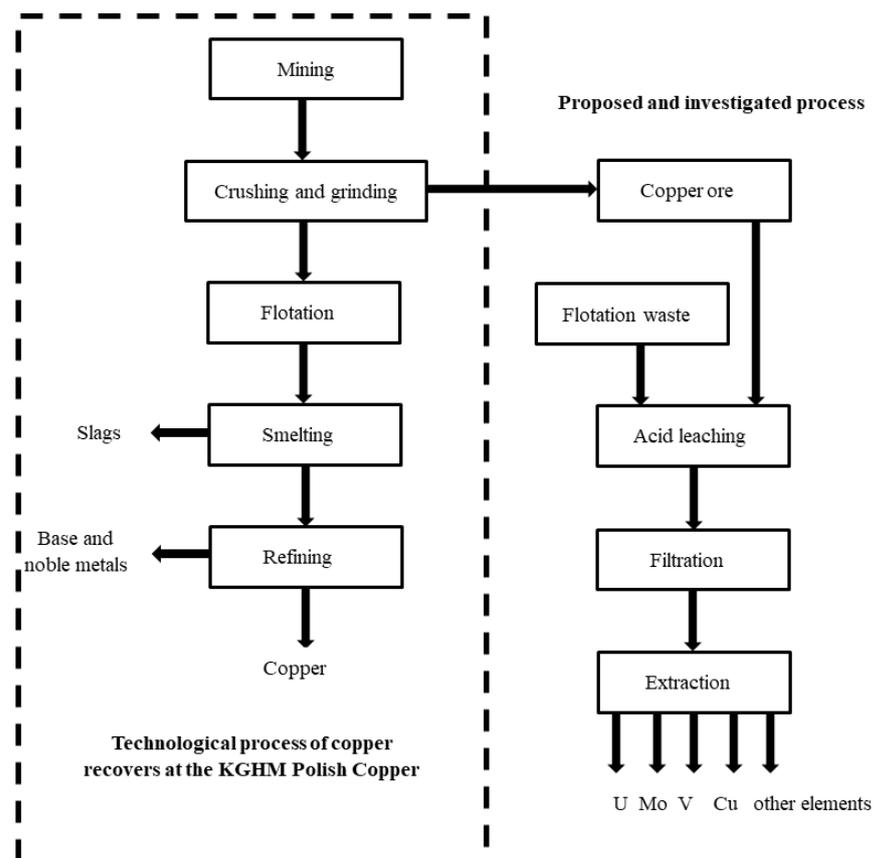


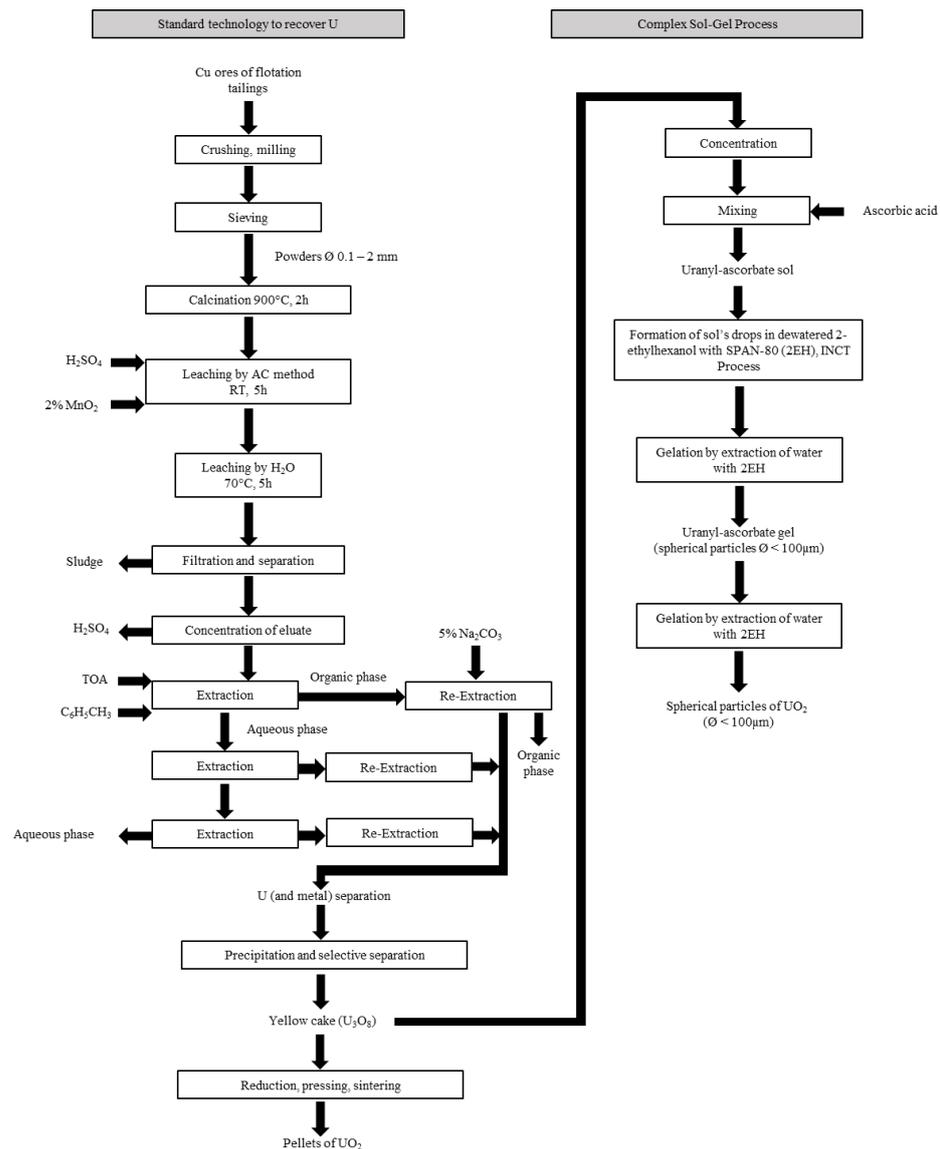
Figure 3. Extraction of Zn from electronic wastes.



**Figure 4.** Process for pyrometallurgical refining of Cu ore and hydrometallurgical recovery of metals from flotation tailings or low-grade Cu ore [62].

In recent years, the INCT has also been researching the potential for recovering U and other elements created as waste products during the manufacture of Cu concentrate from Cu ore [61]. The utilization of the hydrometallurgical processes unlocks the channels for retrieving all the metals present in the liquor. That can be achieved by using a common chemical engineering unit process that is used to recover U and other metals [38]. In situ leach (ISL) processes, in addition to underground and open pit mining techniques, are frequently used to extract minerals such as U. A small amount of U can be extracted as a byproduct of processing Au and Cu ores or deposits of phosphate rock.

Research was carried out on the Polish Cu mining industry, with the prospect of recovering U and rare metals from industrial wastes [38]. In the recovery of U, the commonly used method of precipitation was assessed. The hydrometallurgical recovery processes of U encompassed the application of a concentrated U mixture for the production of spherical particles of  $\text{UO}_2$  by the complex sol–gel process (CSGP), Figure 5. The two hydroxyl sets of ascorbic acids were readily present, including the  $\text{UO}_2^{2+}$  that permits the creation of complexes. The study reported that the combination of both extraction and sol–gel processes had a synergistic impact, which resulted in the design of a reliable scheme for the recovery of U from Cu mining tailings and minerals. For both current and future generations of nuclear reactors, such as pressurized heavy water or fast breeder reactors, a nuclear fuel precursor can be produced using the direct approach of  $\text{UO}_2$  synthesis (with the potential to eliminate the precipitation phase) [38].

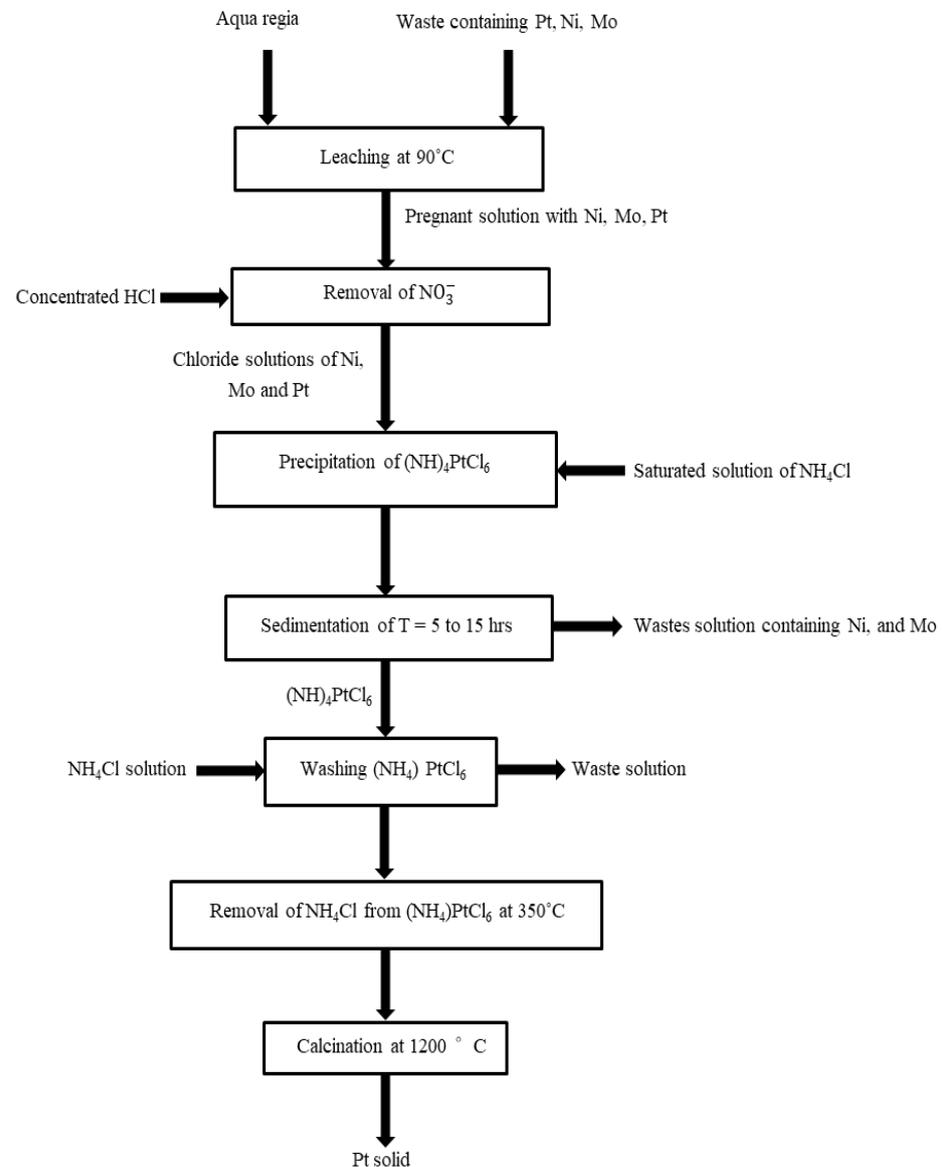


**Figure 5.** Scheme illustrating the hydrometallurgical procedures for extracting (UO<sub>2</sub>) from various sources as described in the INCT complex sol-gel approach [38].

### 3.3. Recovery of the Platinum Group Metals

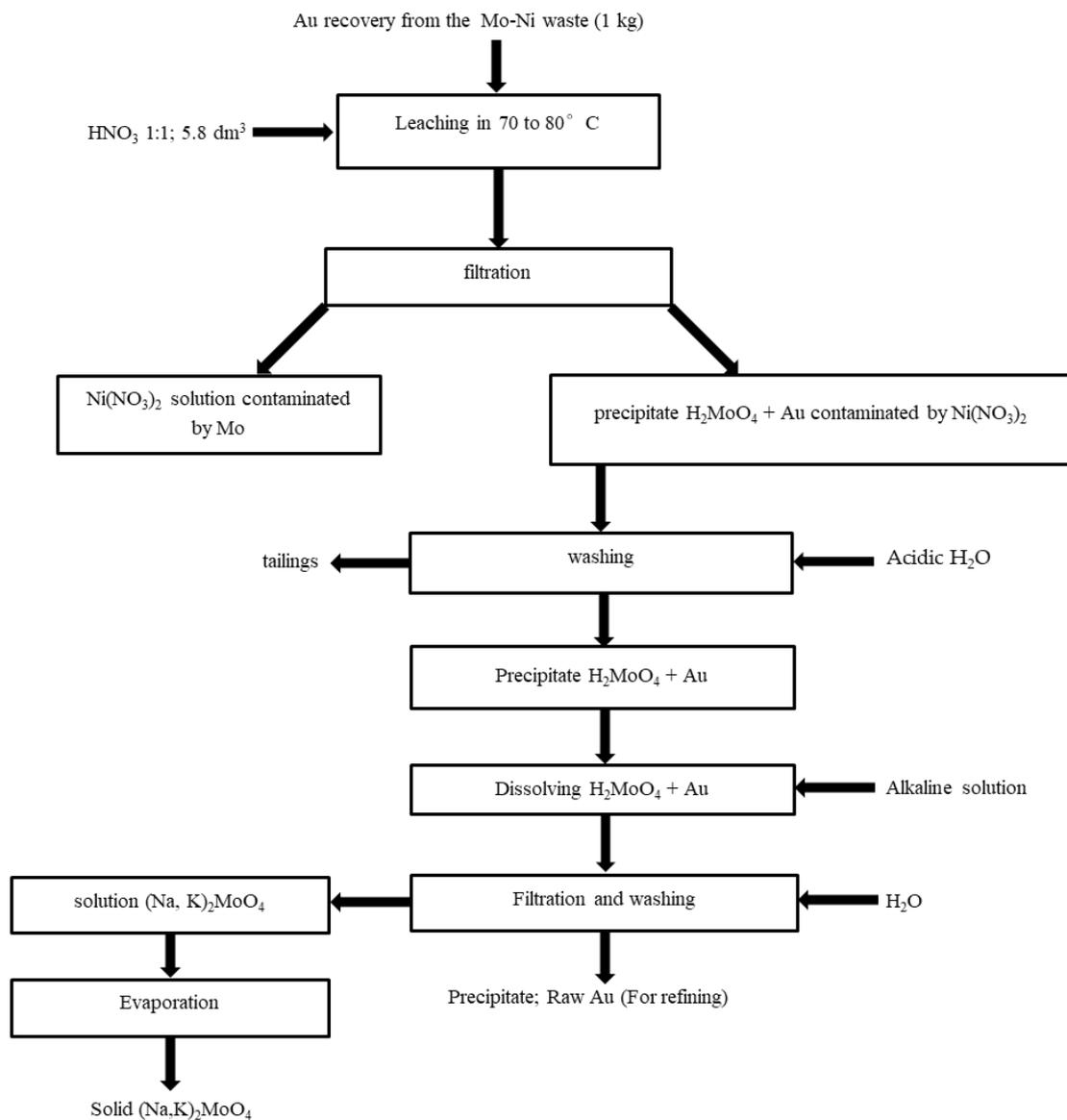
The use of high-grade platinum group metals ore has increased due to their growing industrial demand. Low-grade ore is now more common due to the increasing shortage of high-grade platinum group metals ore. Unluckily, it is prohibitively expensive to extract them from low-grade ore, and doing so raises significant environmental issues. Pt is used as a catalyst in fuel cells to effectively convert O<sub>2</sub> and hydrogen into heat and electrical power. The detection of low Pt levels in biological and environmental samples has been a serious concern with the introduction of Pt-containing catalysts in vehicle exhaust systems. To track the buildup of Pt in the environment, precise and accurate background amounts of Pt in a variety of substances are required. Since Pt is present in sediment samples in such trace amounts, designing techniques to measure it is quite challenging. Developing a process that includes digestion, preconcentration, separation, and Pt detection is an exceptionally effective way to reach incredibly low detection quantities [63]. Utilizing a <sup>191</sup>Pt radiotracer, the kinetics of the extraction of Pt<sup>4+</sup> from an HCl solution applying rubeanic acid in TBP, n-butyl alcohol-acetophenone and thenoyltrifluoroacetone (TPA), were studied [63]. Investigating the effects of acidity, mixing duration, Pt quantity, and back-extraction, the most favorable extraction outcomes for TBP and TPA were obtained

with 4 and 3 M HCl, respectively. INCT in Warsaw also created a method for recovering Pt from the waste solution. Aqua regia was applied as a leaching agent whereas  $\text{NH}_4\text{Cl}$  was used to precipitate Pt for further recovery process, Figure 6.



**Figure 6.** The recovery of Pt from the waste solution.

Apart from platinum group metals, precious metals like Au have drawn a lot of interest [10]. Researchers are attempting to use new techniques in both identification and quantitative analysis. A quantity of 0.02 g of Au is often found in a cell phone [10]. The development and use of alternate hydrometallurgical extraction methods has elevated their significance for many research institutions over the past few decades. Societal concern regarding the environmental impacts of cyanidic Au extraction has increased. The Department of Nuclear Methods of Process Engineering, INCT, Warsaw, carried out the development of hydrometallurgical technologies for the separation of metals from waste. The technological line for the solvent extraction of Au from a mixture of Mo-Ni waste was established in Figure 7.



**Figure 7.** Scheme of Au recovery from molybdenum-nickel waste.

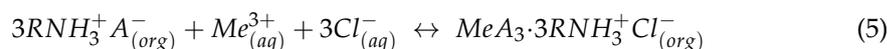
### 3.4. Recovery of Rare Earth Elements

Apatite, xenotime, and monazite are a few of the foremost popular minerals that contain REEs. The extraction and reuse of such minerals from various secondary resources has recently attracted a lot of interest. Considering their secondary origin, various techniques have been carried out to separate them from phosphate or phosphogypsum rocks [64]. Extracting them from the aqueous solution (leachate) is a selective activity. For instance, a mixture of minor actinides (MAs) and REEs was used for the extraction studies. La was removed from MA by employing  $N,N,N',N'$ -tetrakis(4-propenyloxy-2-pyridylmethyl)ethylene-diamine (TPEN) extracting agent. The phase of separation and recovery is intricate and delicate. It is essential to guarantee that each REE separation is highly effective and can be reclaimed at the final stage of the procedure. Knowledge of the extraction characteristics, capacity, phase separation, solubility, selectivity, mass transfer, and economic viability have all been used to develop feasible REE extraction methods [65].

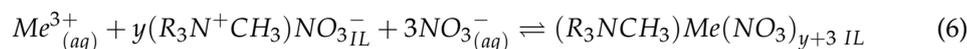
Given their nearly non-volatile nature, low melting point, low flammability, thermal stability, and high ionic conductivity, ionic liquids (ILs) are usually regarded as environmentally friendly solvents and have attracted significant interest. In the extraction of both organic and inorganic materials, ILs made from quaternary ammonium bases and organic

acid moieties are frequently utilized [66]. The benefits of ILs, such as high thermal stability and designability, could potentially be introduced through the use of ILs in the solvent extraction of REEs [67]. Numerous factors, such as the kind of acidic medium, diluent, the temperature of the auxiliary agents, metal ions, contact time, organic-to-aqueous phase ratio, pH, and extractant concentration, can have an impact on the process of solvent extraction. Considering various operational conditions that depend on other factors, a particular operational parameter may have various implications on the desired results [68]. It is challenging to selectively extract and purify REEs from a pregnant solution [69].

REEs' distribution can also be explored by utilizing ILs grounded on phosphinic or phosphoric acids and a metal ion. Due to coordination interactions with moieties of organic and inorganic acids, REEs can produce complex anions (like other metals of side groups). The separation of REEs utilizing an IL based on phosphoric acid and an organic base is represented by Equation (5) [66]:



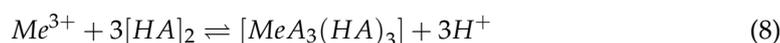
Aliquat 336 can be treated with  $KNO_3$  to exchange  $Cl^-$  with  $NO_3^-$  which improves selectivity over REEs, to reduce the viscosity of the extractant and establish a faster mass transfer. Equation (6) can be used to represent reaction equilibria for A336[ $NO_3$ ] extraction [70].



wherein  $Me^{3+}$  stands for the elemental cation,  $(R_3NCH_3)M(NO_3)IL$  for the IL and metal cation complex, and  $(R_3N^+CH_3)NO_3^- IL$  for A336[ $NO_3$ ]. IL stands for both the IL phase and the aqueous phase. The equilibrium constant  $K_{eq}$  is expressed as follows:

$$K_{eq} = \frac{[(R_3NCH_3)Me(NO_3)_{y+3} IL]}{[Me_{(aq)}^{3+}][(R_3N^+CH_3)NO_3^-_{IL}]^y [NO_3^-_{(aq)}]^3} \quad (7)$$

Equation (8) may be employed to express the reaction equilibrium for D2EHPA separation.



whereby  $Me^{3+}$  stands for the metal cation,  $[HA]$  for the organic phase's extractant, and  $[MeA_3(HA)_3]$  for the complex of the extractant and metal. The equilibrium constant  $K_{eq}$  is expressed as follows:

$$K_{eq} = \frac{[MeA_3(HA)_3][H^+]^3}{[Me^{3+}][(HA)_2]^3} \quad (9)$$

The separation of REE such as La can be accomplished using the IL [A336][CA-12] in chloride media. Additionally, it was demonstrated that IL[A336][P507] was suited to separate light REEs in chloride media and would work for the isolation of heavy REEs in nitrate media. By applying IL [A336][P507], the  $Ce^{4+}$  and  $F^-$  ions have been effectively extracted from  $H_2SO_4$  solutions and separated [67]. The recovery of mid-heavy REEs in  $H_2SO_4$  solution by [A336][P507] became the subject of a thorough examination. According to the findings, temperature, extractant concentration, and pH all boosted the rate of REE extraction [67]. The results demonstrated that, as both the temperature and extractant concentration increased, so did the distribution ratios of REEs. The influence of pH on the separation behaviors of  $Tb^{3+}$  by Cyanex 923, IL [A336][P507], TBP, and P350 (di-(1-methylheptyl)methyl phosphite) is important. Its recovery by Cyanex 923 and TBP in systems of pH = 1.0 to 0.7 improved with rising acidity. At pH < 0, P350 showed a comparable tendency as Cyanex 923 and TBP. Following a reduction in acidity, the  $Tb^{3+}$  was extracted more effectively. IL [A336][P507] is more appropriate for the separation of REEs at low acidity, as evidenced by the divergence in recovery performance [67].

Because of the salting-out phenomenon found in the extraction of  $\text{Lu}^{3+}$ , the recovery of REEs decreased as the concentration of  $\text{Na}_2\text{SO}_4$  increased. The process of extraction was hindered by the binding of such cations with  $\text{SO}_4^{2-}$  in the aqueous medium. However, as the concentration of  $\text{NaNO}_3$  or  $\text{NaCl}$  increased, the yield of extraction rose as well. The different behaviors of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  complexes could be caused by the ion connection between anions and  $\text{REE}^{3+}$ , and the hydration effect. A decline in the recovery of metal ions results from the generation of  $\text{REESO}_4^+$  ions at high sulphate amounts. It is understood that leaching agents for REEs ores of the ion-adsorbed class once included  $\text{NH}_4\text{NO}_3$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $(\text{NH}_4)_2\text{SO}_4$ .  $\text{NaCl}$  was likewise the first leaching solvent to be widely utilized. As the concentration of  $\text{NaCl}$  grew, so did the effectiveness of REEs' extraction. The above extraction technique is more effective in extracting mid-heavy REEs than the aqueous medium devoid of  $\text{NaCl}$ .  $\text{Al}^{3+}$  and  $\text{La}^{3+}$  experience low extractability as a result, allowing this technique to be employed to retrieve mid-heavy REEs from the pregnant solution. Following a rise in the concentration of  $\text{NaNO}_3$ , the distribution ratios of all REEs rose, particularly for the mid-heavy REEs. The mixture with  $\text{NaNO}_3$  has a substantially higher extractability than the one employing  $\text{NaCl}$  [67].

With heating, the precipitated form of Th and REEs such as Ce created after the recovery process can be dissolved in 4 M  $\text{HNO}_3$ . Th can be obtained by extracting it with Aliquat 336 diluted in kerosene, stripping it with HCl solution while agitating, and precipitating it as ammonium hydroxide.  $\text{Ce}^{3+}$  is, on the contrary, oxidized into its tetravalent form by the incorporation of sodium bromate. It can then be recovered by Aliquat 336 in kerosene that contains 1-octanol, stripped by shaking the organic solution with diluted  $\text{HNO}_3$  media, and finally precipitated as hydroxide using ammonia. La, Nd, and Y-rich aqueous media can be treated at 25 °C by a synergistic TRPO-TOPO combination in kerosene with a 2:1 O/A phase ratio.  $\text{H}_2\text{SO}_4$  can then be applied to strip the organic media in an equimolar ratio to isolate the majority of the Y, after which, HCl is used as a stripping agent to retrieve Nd and La [71].

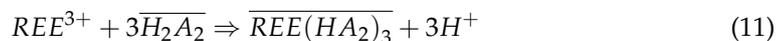
In nitrate medium, REEs (Sm and Nd) were extracted from discarded fluorescent lamps using Cyanex 923, which serves as a solvating extractant. Researchers noticed that, although the co-extracted metals took longer than 15 min to reach a state of equilibrium, the REEs did so in just one minute. For greater REE recovery, they recommended low acidity (less than 1 M  $\text{HNO}_3$ ), one minute of reaction time in between the two phases, up to 1 M extractant concentration, stripping with 4 M  $\text{HNO}_3$ , and scrubbing by  $\text{HNO}_3$  or oxalic acid. The REE metal ion was extracted from Nd-Fe-B magnet residue using solvent TBP in IL (Aliquat 336). To improve the distribution coefficient throughout the REE recovery from Ni metal hydride batteries employing chloride medium,  $[\text{A336}]\text{NO}_3^-$  and Cyanex 923 were utilized [52].

To remove REEs and transition metals from Sm/Co and Nd/Fe magnets, Cyphos IL 101 was implemented. Scientists discovered that transition metals are efficiently extracted by the IL, and the maximum distribution rates for Co and Fe, respectively, were attained with 8.5 M and 9 M HCl. The separation coefficients for Sm/Co and Nd/Fe were discovered to be  $8 \times 10^5$  and  $5 \times 10^6$ , respectively. Transition metals including Co, Mn, Fe, and Zn could additionally be extracted using Cyphos 101 IL from an aqueous media that also contains REEs and Ni with 8 M HCl. Following the initial extraction stage, Cyanex 923 and Aliquat 336 nitrate were employed to recover the REEs from the raffinate. Because Aliquat 336 nitrate is more selective for REEs and can handle less Cyanex 923 molecules around it than Cyphos 101, it is preferred over the latter. A336 chloride and A336 thiocyanate were applied to separate Co and Mn. It was possible to recover La from Ni and Sm from Co through the application of trihexyl (tetradecyl) phosphonium nitrate. REEs were successfully recycled using this technique from used permanent magnets and rechargeable batteries. Here, they added Na or ammonium nitrate to the aqueous media, and the consequence of salting out caused the extraction to improve. They discovered that Sm could be extracted as the pentakis complex  $[\text{Sm}(\text{NO}_3)_5]^{3-}$  and La as the hexakis complex  $[\text{La}(\text{NO}_3)_6]^{3-}$ .  $\text{H}_2\text{O}$  was the medium used to do the stripping [52].

Synergistic extraction of REEs can offer the benefit of using reduced usage of the main extracting agent, while still being able to achieve a high rate of separation and replenish the extracting agent. TBP and D2EHPA are two of the most popular and commonly employed of these in the commercial process for the extraction of REEs. Although TBP has a higher loading capacity for REEs compared to D2EHPA, D2EHPA possesses a superior separation coefficient for REEs. An assessment was conducted on the impact of the aqueous phase's concentration of  $\text{NO}_3^-$  and  $\text{H}^+$  ions. Also, an evaluation was conducted on the kind and number of extracting agents present in the organic phase, and on the extraction behavior of La, Nd, Ce, and Y. An organic phase comprising 0.8 M of extracting agents with an equal mole ratio of D2EHPA and TBP in kerosene was employed to test the influence of the  $\text{NO}_3^-$  ion concentration on the recovery of REEs. The concentration of  $\text{H}^+$  ions in the aqueous media was set at 2 M (pH = -0.3). As the amounts of  $\text{NO}_3^-$  in the aqueous medium increased, the recovery of REE was reported to rise as well. In comparison to the other examined REEs, Y exhibited a higher extraction efficiency. Therefore, when the amount of  $\text{NO}_3^-$  ions rises, so do the distribution ratios of REEs. A sharp increase in the Y distribution ratio over 6 M  $\text{NO}_3^-$  was observed. Because the  $\text{REE}^{3+}\text{NO}_3^-$  species were removed following the recovery mechanism of REEs by TBP, which is determined according to the reaction in Equation (10), a common ion effect could potentially be responsible for the rise in extraction caused by an increase in  $\text{NO}_3^-$  ions concentration [69].



With an increase in the concentration of  $\text{H}^+$  in the aqueous media, the distribution coefficient of REEs dropped. Relative to other REEs, Y is particularly susceptible to changes in the concentration of  $\text{H}^+$ . The cation exchanger extracting agent D2EHPA's recovery mechanism is capable of being used to illustrate how  $\text{H}^+$  affects REEs extraction. Below is the equation showing the extraction mechanism of REEs from aqueous media using D2EHPA:



### 3.5. Precipitation

The extracted metals can be recovered in solid form by precipitation. This is realized through the combination of selected ion(s) with an appropriate counter ion in adequate concentrations to surpass the subsequent compound's solubility product and produce a supersaturated solution. Precipitation occurs at lower temperatures, low ion concentration, a high degree of supersaturated solutions, and a minimal stirring of the solutions. The size of the precipitate depends on the type of solvent and pH of the solutions. Metals from sources such as acid mine drainage are normally precipitated as metal oxides, phosphates, sulfides, hydroxides, and carbonates [72].

The precipitation technique is easy to control, simple, inexpensive, and applied in industry. Double-salt precipitation, simple precipitation, and oxidative precipitation are the techniques utilized in hydrometallurgy for secondary resources and primary ores. In simple precipitation, precipitants such as  $\text{OH}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{S}^{2-}$ , and  $\text{CO}_3^{2-}$  are applied [73]. Generally, double-salt precipitation entails the use of salt with more than one anion or cation. Double-salt precipitation is crucial in the recovery of REEs. When some compounds are precipitated or eliminated from a solution by oxidation, the term "oxidative precipitation" is generally used. In other cases, some metal ions can be precipitated by adding complexing agents to form complexes when ligand ions or ligand molecules are available [73]. In most cases, a complexing and precipitating agent can be used together for improved and selective recovery of a metal such as Ni, Mn, Co, Cu, and Fe. For such metals,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{S}^{2-}$  precipitants combined with  $\text{NH}_3$  as a complexing agent are effective in complexation-precipitation.

### 3.6. Ion Exchange

Ion exchange is among the separation techniques that play a big role in the recovery of a wide range of metals with unique properties suitable for the current and future economy. Due to intense mining activities, metals have significantly reduced in ores, and they exist in low concentrations. The ion exchange technique is suitable for the recovery of such metals. That is attributed to its environmental safety, selectivity, powerful resolving ability, high efficiency, moderate cost, and suitability for combination with subsequent techniques in the recovery of noble metals and other applications [74,75]. Ion exchangers with distinct functional groups, due to their good kinetic properties, high mechanical strength, and exchange capacity, increase their suitability in the concentration of microscopic amounts of metals, extracting them in the presence of accompanying components.

Ion exchange resins acting like porous media are essential in separation industries because of the elimination of thermal regeneration, a higher metal ion loading capacity, higher loading rate, and being less prone to fouling by organic materials. The porous property of the resin leads to enhanced adsorption rates because of the improved diffusion of the ions. The metal recovery process's efficiency is firmly reliant on the contact time, pH of the solution, ion concentration, and ion coordination/exchange resin properties such as structure and type of the ligand, crosslinking degree, and swelling [76]. Various types of exchange resins are available commercially in the recovery of metals; for example, Amberlite IR-120 can be used in separating  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$ . Chelating ion exchange resins such as Amberlite IRC 748 and Chelex 100 have aminodiacetic acid functional groups to exchange  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  from aqueous solutions while macro-porous AMBER JET 1200 Na cation exchange resins are efficient in the separation of metals such as  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  [77]. In the recovery of platinum group metals such as  $\text{Pa}^{2+}$ ,  $\text{Pt}^{2+}$ , and  $\text{Pt}^{4+}$  from HCl acid solutions, CYBBER and Purolite grades present high sorption capacity for the anion exchange [74].

## 4. Recovery of Strategic and Critical Metals Using Flotation

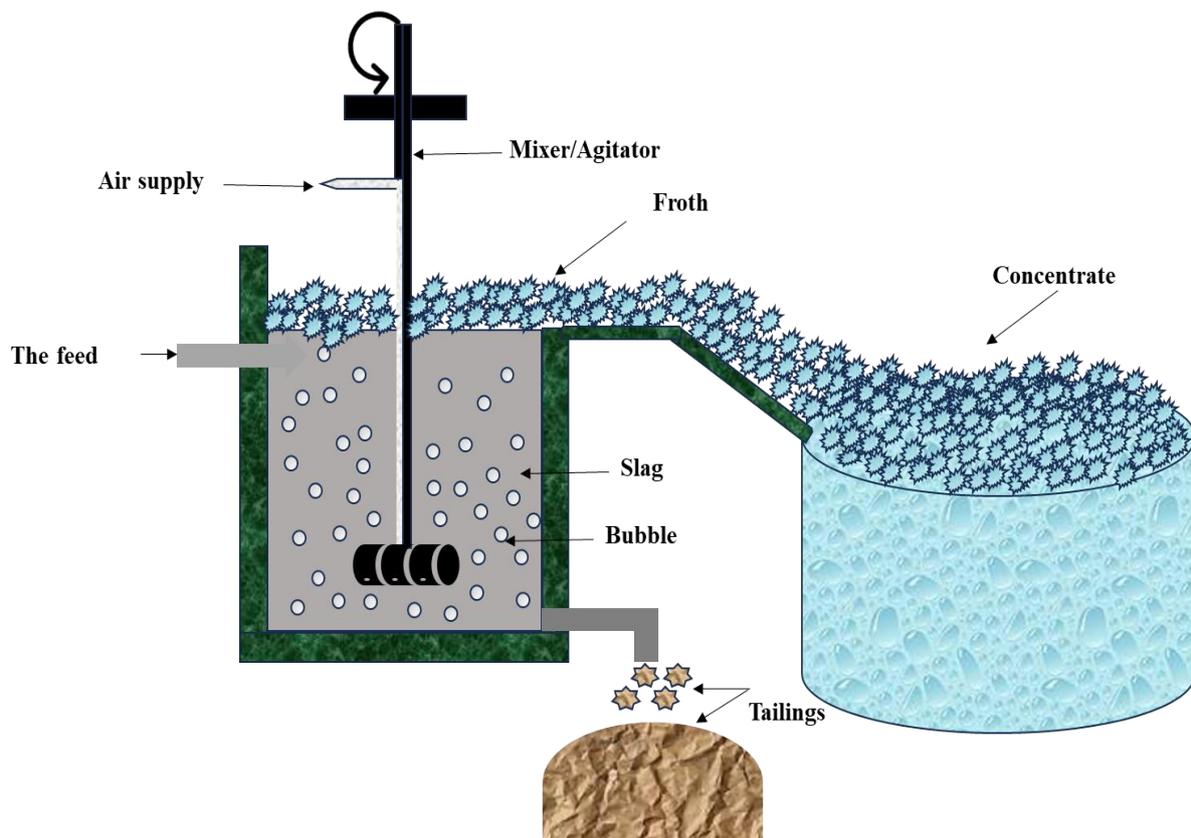
Flotation is essentially a surface selectivity-based extraction method that separates the hydrophilic portion of a material from the hydrophobic portion. To create a wide range of separations, this technique selectively modifies the hydrophobicity of the mineral surfaces using several surfactant chemicals [27]. While gangue minerals—unwanted minerals—remain in the water, the target minerals, which are frequently sulphide minerals, are usually hydrophobic and will adhere to the air bubbles [78–82]. The subsequent froth rich in minerals is subsequently scraped off the flotation cell's surface, Figure 8.

If flotation techniques used in other regions are tailored to suit the current minerals, they will be essential for the beneficiation of the minerals in Kenya. Research was conducted to recover Cu and Co by treating the tailings from the flotation of Cu and Co oxidized ores produced at the Kambove Concentrator (DRC). The study focused on determining the dosage of chemicals needed to float the examined tailings and recover the maximum amounts of Cu (44.80%) and Co (88.30%). Centered on the concentrate grade (3.31% Cu and 2.22% Co) and the feasible extraction of the metals of interest, it was determined that flotation was a desirable method for reprocessing the tailings [83]. The tailings from the processing of Cu ores contain rocks that may be recycled as inexpensive raw materials. The overconsumption of reagents due to the particle size distribution in a wide range of slimes is still an obstacle. Such an issue should be taken into consideration for the most effective technical and financial implementation of the aforementioned technique. While the wastewater produced by the flotation of tailings can be reclaimed and fed back into the Kambove Concentrator milling process, the tailings can be added to construction materials as cemented pastes [83].

Slags are also known to have valuable metals, and instead of being an end waste, they can serve as a secondary source of metals [84,85]. They come in a variety of forms, as wastes from combustion processes or as the results of metallurgical operations. They have been used in numerous fields as a resource material [85]. Furthermore, for certain purposes,

the characteristics of slags are as good or better than those of competing materials. From nonferrous smelters, a range of nonferrous slags are generated.

Numerous investigations on metal recovery using nonferrous slags have already been conducted. A large number of studies focused on recovering metals from Cu slags [85,86]. By considering variables, including the form of the processed ore, the kind of furnaces employed, and the cooling techniques, the chemical composition of Cu slags from various sources might range significantly. The main phases in crystalline Cu slag are often fayalite and various silicates. Most of the time, Ni and Co are found as oxides where the Co distribution in the slags is extremely homogeneous. On the other hand, many Cu slags have diverse types of Cu minerals. They could take the shape of oxides, sulphides, or a combination of the two. Investigations were conducted on the recovery of Cu and Co from ancient Cu slags collected from the Küre Plant basin of Turkey [86]. The slag was of the fayalitic kind, which contained 1.24% Cu, 53.16% Fe, and 0.53% Co. To retrieve the metal values, two distinct paths were taken. The first method was leaching it after roasting it with pyrite ( $\text{FeS}_2$ ). The second method involved leaching, and roasting the flotation tailings with  $\text{FeS}_2$ , followed by flotation of the slags. It was discovered that the second method worked well for treating the Cu slag. During the flotation process, a Cu concentrate with around 11% Cu was created, and 77% of the Cu was recovered, leaving 93% of the Co in the tailings [86].



**Figure 8.** A sketch of the froth flotation process.

Due to the small amounts of platinum group metals in primary ores (less than 10 g/ton) and the complex processes involved, their extraction from primary ores is costly. Ores (such as Merensky Reef ore grades, which comprise 3 to 8 g/t platinum group metals tied to Ni, Cu, as sulphides) are mined, ground, processed through gravity separation, and floated. Their concentrate, which is generally 200 to over 2000 g/t platinum group metals alongside 0.4% to 2.8%  $\text{Cr}_2\text{O}_3$ , undergoes meltdown at excessive temperatures ( $>1500\text{ }^\circ\text{C}$ ). Thereafter, they are purified through hydrometallurgical processes [87]. Traditionally, froth flotation

has been used to extract platinum group metals from pure (unweathered) sulphide ores. This method usually yields recoveries of over 85% for Pt. The efficient concentration of such metals through flotation in virgin sulphide ores is dependent upon the presence of highly floating base metal sulphide minerals, such as pyrrhotite, chalcopyrite, and pentlandite. Nevertheless, as an alternate source for keeping up their production, the rapid depletion of sulphide platinum group metal-bearing minerals has sparked a lot of interest from scientists. The focus has been on investigation of their recovery from near-surface oxidized metal ores.

Besides platinum group metals, Au can be extracted using the flotation technique [25,43]. Au floats easily, and it is possible to separate free Au from sulfide-containing ore via selective flotation. A product that is directly smeltable could potentially be produced by removing the floating Au from the sulphides. According to research, selective flotation of Cu sulphides could be observed from FeS<sub>2</sub> ores at pH values higher than 11 [88]. The behavior of the free Au in these circumstances was less obvious. Additional collectors (monothiophosphates) could be included for increased Au recovery because they are known to be selective Au accumulators [88,89]. Researchers looked into how several operating factors, such as pH, collector additions, and grind size, affected the efficacy of Au flotation [88]. With a variety of collectors, Au was recovered selectively against FeS<sub>2</sub> at elevated pH levels. Nevertheless, in the flotation tests, there was no specificity towards chalcopyrite. Granular Au drifted towards the flotation tail, but fine Au floated more readily. That is because the flotation of Au is highly dependent on some parameters like the type of the collectors, size, structures, and the mineral containing Au, amongst others.

Numerous studies have also been conducted to examine the dynamics of flotation of REEs in terms of pulp chemistry, froth stability, mineral particle size distribution, and collector–mineral surface interactions [90]. The flotation effectiveness of REEs is measured by the flotation rate test, which considers concentrate grade, mass pull, and recovery. The flotation kinetics of the mine is defined as the fluctuation in the recovery of metals over time. The outcomes are utilized to characterize a mineral's flotation behavior in specific flotation conditions. The flotation rate of the REEs depends on the length of flotation, pulp pH, the kind and dose of the collector, the extent of surface–collector contact, and the mineral species. The principal materials that are the primary industrial sources of REE minerals are monazite (REE)PO<sub>4</sub> (55 to 60% RE oxides), xenotime (REE)PO<sub>4</sub> (55 to 60% RE oxides), and bastnaesite [REE(CO<sub>3</sub>)]F (70 to 75% RE oxides). Flotation is considered to be one of the most essential methods for separating REEs from related minerals and producing concentrates. The resulting material often contains 60 to 70% mixed REEs, due to the intricate and fine properties of the REE ore [91].

The assessment was done on the flotation of rare earth oxide (REO) in monazite by combining hematite (Fe<sub>2</sub>O<sub>3</sub>) and quartz (SiO<sub>2</sub>) with hydroxamic acid [90]. The results of the micro-flotation experiments carried out on individual minerals demonstrated that each model mineral's flotation response depends on pH. The optimal flotation extraction of quartz happened at pH = 3, while that of hematite and monazite was attained at pH = 7. As predicted, adding more hydroxamic acid increased each mineral's flotation yield. When the dose of hydroxamic acid was increased, the specificity coefficients of monazite over quartz remained lower than those of monazite against hematite. In a mixed minerals flotation, it was anticipated that a higher percentage of Fe<sub>2</sub>O<sub>3</sub> would be associated with REO in flotation concentrates than SiO<sub>2</sub>. The outcome suggested that depressants are necessary to accomplish selective beneficiation and extraction of REO. Further results on heterogeneous minerals separation experiments demonstrated that, in the absence of depressants, the flotation of REO from SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> was unselective. It was reported that 96% Fe<sub>2</sub>O<sub>3</sub>, 99% REO, and 80% SiO<sub>2</sub> recoveries of the concentrate were produced by a 2000 g/t hydroxamic acid collector. Whenever 4000 g/t starch was employed, the extraction effectiveness of REO rose from its low average of 6.42% devoid of depressants to 44.78%. Matching recoveries of 93% REO, 38% SiO<sub>2</sub>, and 81% Fe<sub>2</sub>O<sub>3</sub> were observed. Contrarily, when Na<sub>2</sub>SiO<sub>3</sub> was utilized, the resulting concentrates had greater gangue contents (SiO<sub>2</sub> > 60% and Fe<sub>2</sub>O<sub>3</sub>

> 90%). That resulted in lower REO separation efficiency. When hydroxamic acid was present, starch provided a better REO upgrade. Nevertheless,  $\text{Na}_2\text{SiO}_3$  was a better choice when REO recovery was the only factor considered. Furthermore, a mixture of starch and  $\text{Na}_2\text{SiO}_3$  demonstrated considerable recoveries [90].

The beneficiation reaction of gangue minerals and REE in the tailings differs noticeably. The separation techniques of froth flotation, wet magnetics, and gravity led to widely differing REE upgrades and recoveries. A flotation study was conducted on the ore by applying sodium oleate acting as a collector. To determine if there was a possibility of extracting and enriching REE minerals in saprolite ore, a study examined three distinct treatment configurations: the relative impacts of pulp pH, depressants, and de-sliming. Most REE minerals (>50%) could be extracted using flotation methods on raw feed. However, the technique was not selective, given that clay minerals and silicate gangue also found their way into the flotation concentrate together with the REE minerals. The specificity of the flotation of REE minerals was enhanced by de-sliming before flotation, using a mixture of depressants ( $\text{Na}_2\text{SiO}_3$  and starch). That resulted in concentrates that had total REO grades of 5.87% and 4.22%. Recovery yields of 45% and 50% at pulp pH = 9 and 10.5 were obtained. Because of their fine-to-ultrafine properties, clay gauge and silicate minerals were collected through the synergistic process of surface activation and entrainment. A random grade–recovery relationship was found when all test results were compared. It indicated that there could be a need for more flotation tests where its process limitations can be looked into. Optimization is also necessary to further maximize both REE recovery and grade. Additionally, the possibility of employing magnetic separation was raised [92].

Apart from the physical methods, ILs have been seen as revolutionary in the flotation of REEs. Tetraethylammonium mono-(2-ethylhexyl)2-ethylhexyl phosphonate ([N2222][EHEHP]) is an IL that has been studied earlier for REE solvent extraction and revealed to be selective and efficient. For the first time, [N2222][EHEHP] was assessed as a collector in bastnäsite flotation, which is the main deposit for producing REEs [93]. The findings were contrasted with two typical gangue minerals found in quartz and hematite. Hematite exhibited an enhanced collectability of [N2222][EHEHP] over bastnäsite, which significantly recovers at pH = 5 with an increased dosage of IL (500 g/t). It implies that these minerals' extraction mechanisms could not be the same. Based on the Fourier transform infrared spectroscopy (FT-IR) data, [EHEHP] moiety adsorption on bastnäsite was verified. It seemed to be most effective in slightly acidic pH conditions. The micro-flotation data, which indicated that bastnäsite recovery was maximum (~50%) at pH = 5, was consistent with this. Furthermore, micro-flotation indicated that a very high dose of IL must be administered to directly float bastnäsite. Protons may interact with [EHEHP]<sup>−</sup> and obstruct interactions between REE ions and [EHEHP]<sup>−</sup>, which explains why bastnäsite flotation recovery is lower at pH = 3. According to FT-IR data, the adsorption of the [EHEHP]<sup>−</sup> moiety on hematite is evident in acidic conditions, which matches the micro-flotation recovery pattern. Furthermore, hematite may be more recoverable because of its better yield compared to bastnäsite. The little recovery for quartz at both dosages across the pH range under test signified the absence of reagent adsorption. By using magnetic separation to examine the concentrates and tails, it was discovered that higher collector dosages might result in bastnäsite recovery capacities over 90% and an optimal conversion ratio of 1.7 [93].

## 5. Proposals and Prospects for Future Application of the Hydrometallurgical and Flotation Techniques

In 2016, Kenya implemented the Mining Act meant to modernize and expand the mining industry. Even though the Act was improved from the previous legislation, output in the mining sector remains poor. However, the new regime announced the removal of the moratorium in 2023. The Government emphasized the importance of creating a good business atmosphere for stakeholders and investors. Kenya's future development of the mining sector will be influenced by environmental impact and the adoption of sustainable mining techniques. Given the rising number of international mining firms promising to decarbonize and achieve net zero goals, the mining sector should develop practical

approaches to tackle environmental issues in their operations. The approach will compel investors to apply environmentally justifiable techniques for metal recovery.

As Kenya seeks to diversify its mining practices, hydrometallurgical and flotation procedures emerge as a compelling alternative. These innovative approaches will not only address the constraints posed by low-grade ores but also align with global sustainability goals. Through investment in research and regulatory and infrastructure adaptations, Kenya can pave the way for a dynamic and responsible mining sector. That will contribute to both economic development and environmental preservation.

The metal recovery techniques outlined in this article can easily be applied to the needs of the Kenyan mining industry. The development of advanced leaching technologies can enhance the efficiency and selectivity of metal extraction. Continuous research and investment in these technologies can optimize the recovery of strategic and critical metals. One of the challenges in Kenya's mining industry is the presence of low-grade ore deposits. Hydrometallurgy offers a viable solution, enabling the cost-effective extraction of metals from ores that were previously considered economically unviable. Such an option becomes crucial in times of depleted mineral reserves for important metals, when alternative sources must be explored. Beyond primary ores, hydrometallurgy provides an avenue for recovering metals from secondary sources. With the growing demand for recycling and a circular economy, Kenya can leverage hydrometallurgical procedures to extract valuable metals from secondary sources, contributing to resource sustainability. The mining research institutions in Kenya will need to also initiate progressive efforts to enhance the efficacy of the flotation process. That could encompass the implementation of advanced control systems or the formulation of improved surfactants.

There will be a need for the establishment and demonstration of pilot plants to exhibit the effectiveness and feasibility of the described methods. That can be reinforced by introducing capacity-building programs and training dynamism, to equip local experts with the knowledge required to operate flotation and hydrometallurgical processes. Collaboration with research institutions, both domestically and internationally, can fast-track the development of competent and environmentally friendly metal-recovery processes tailored to the country's mineral resources. In addition, regulatory frameworks ought to be adapted to address the drawbacks and opportunities associated with chemical-based techniques for metal recovery. Clear guidelines, environmental impact assessments, and monitoring mechanisms should be established to foster responsible mining practices.

## 6. Conclusions

The vast unexploited mineral resources in Kenya present a major opportunity for economic development. Nonetheless, the environmental impacts of mining in the region cannot be neglected. Mineral extraction processes require a well-adjusted approach that considers both sustainability and economic returns. The adoption of modern flotation and hydrometallurgical methods emerges as an important solution to efficiently extract strategic and critical metals while reducing environmental effects. For full balance in society of a sustainable and new world, we must not forget about people. Skillful management of natural resources and investment in local communities should guarantee stable and peaceful development. The mining industry and government stakeholders must adopt sustainable technologies, while prioritizing responsible mining practices. All-inclusive and collaborative steps are necessary for harnessing Kenya's potential mineral wealth, while protecting the delicate balance of its environment.

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